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ON RAMMELSBERGITE AND PARARAMMELSBERGITE: DISTINCT FORMS OF NICKEL DIARSENIDE

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ABSTRACT

Rammelsbergite from Eisleben and Schneeberg (type locality) is orthorhombic; space group D_{2h}^{12} — Pmn ; $a_0=3.53$, $b_0=4.78$, c_0 (fibre axis) $=5.78\text{\AA}$; twin plane (110); cleavage {110}; unit cell contains $2[\text{NiAs}_2]$; $G=6.97$ (meas.), 7.05 (calc.); the structural data are similar to those of marcasite. A new analysis is given.

Pararammelsbergite from three mines in Ontario is orthorhombic (or pseudo-orthorhombic); apparent holohedral space group D_{2h}^{11} — $Pbma$; $a_0=5.74$, $b_0=5.81$, $c_0=11.405\text{\AA}$; twinning not seen; cleavage {001}; unit cell contains $8[\text{NiAs}_2]$; $G=7.12$ (meas.), 7.24 (calc.).

In polished sections both minerals are hard, white and strongly anisotropic, with perceptible differences in habit, twinning, polarization colours, and resistance to moist air. They are easily distinguished by their unlike x-ray powder patterns.

INTRODUCTION

The existence of an orthorhombic form of nickel diarsenide, as distinct from the cubic mineral of similar composition, was suspected by Breithaupt (1835) and later confirmed by the same author (1845). For the orthorhombic mineral Breithaupt retained the early name *Weissnickelkies*, proposing *Chloanthit* for the cubic modification. Haidinger (1845) introduced the name *Rammelsbergit* for *Weissnickelkies*, without recognizing the orthorhombic symmetry. This caused some confusion of nomenclature which was rectified by Dana (1845), whose use of rammelsbergite for the orthorhombic mineral, and chloanthite for the cubic species, was generally accepted.

The characterization of rammelsbergite still rests mainly on Breithaupt's description (1845) of the indistinctly crystallized mineral from Schneeberg, Saxony, and Riechelsdorf, Hesse. Later reported occurrences, particularly in the Cobalt and South Lorrain districts of Ontario (Walker and Parsons, 1921; Walker, 1925; Thomson, 1930) have confirmed the individuality of a presumably orthorhombic mineral with the essential composition NiAs_2 and have yielded the valuable mineralographic characters summarized in Schneiderhöhn and Ramdohr (1931) and Short (1934).

The specific description of rammelsbergite remains incomplete, however, for lack of accurate crystallographic or structural data. The scanty goniometric observations of Breithaupt (1845), Palache and Wood (1904), and Dürrfeld (1911), all made on small, poor crystals, show no agreement; nor does the isolated suggestion by De Jong (1926), that rammelsbergite is structurally the same as loellingite, carry conviction.

An effort was therefore made to obtain single crystal *x*-ray measurements on rammelsbergite in order to determine the symmetry, cell dimensions and cell content of the species and to find its systematic position. The single European specimen at first available, from Schneeberg, offered no hope of obtaining a measurable crystal. Canadian specimens were therefore studied, and eventually the desired information was obtained on material from Gowganda and Cobalt, Ontario, with the chemical and physical properties of rammelsbergite (Peacock and Michener, 1939).

But again the new crystallographic data showed no agreement with any of the previous observations; and therefore the description of the Canadian mineral was concluded with the statement:

At present we can say that if rammelsbergite is defined as the orthorhombic or pseudo-orthorhombic diarsenide of nickel, then our material is rammelsbergite of unusual purity; if it can be shown, however, that the original or typical rammelsbergite (if such can be obtained) is a homogeneous mineral essentially different from ours, then the Ontario mineral is a distinct substance.

Further work on this problem confirmed the second of the foregoing alternatives. Specimens from Eisleben, Thuringia, gave complete data which certainly refer to rammelsbergite, as shown by the chemical composition, physical properties, and above all the *x*-ray powder photograph, all of which are the same as those of rammelsbergite from Schneeberg. The structural data of the Canadian mineral bear no simple relation to those of rammelsbergite or of smaltite-chloanthite. The Canadian mineral previously named rammelsbergite is therefore a distinct species for which the name *pararammelsbergite* was recently proposed (Peacock, 1939); this name alludes to the fact that the composition of the new mineral is the same as that of rammelsbergite.

The principal object of the present paper is to give the new observations on rammelsbergite from Eisleben and Schneeberg. To establish the individuality of pararammelsbergite the essential properties of the Canadian mineral will be restated, together with some further observations. The name pararammelsbergite may thus be considered to apply retroactively to the mineral already described in detail by Peacock and Michener (1939).

MATERIALS AND ACKNOWLEDGMENTS

The following specimens served as the basis of the present study:

1. Rammelsbergite, Royal Ontario Museum of Mineralogy, M/4036, Schneeberg, Saxony, Germany (type locality).
2. Rammelsbergite, ROMOM, M/19708, Eisleben, Mansfeld district, Thuringia, Germany.
3. Rammelsbergite, United States National Museum, C-693, Eisleben, Mansfeld district, Thuringia, Germany.
4. Pararammelsbergite, ROMOM, M/12411, Moose Horn Mine, Elk Lake, Gowganda, Ontario (specimen 1 in Peacock and Michener, 1939).
5. Pararammelsbergite, ROMOM, M/11772, Hudson Bay Mine, Cobalt, Ontario (three specimens); 5a (specimen 2 in Peacock and Michener, 1939) is almost pure pararammelsbergite, 5b and 5c contain visible amounts of other white metallic ores.
6. Pararammelsbergite, ROMOM, M/14242, Keeley Mine, South Lorrain, Ontario.

The specimens from the Royal Ontario Museum were kindly made available for study by Professor A. L. Parsons. The specimen from the United States National Museum is a fragment representing material analyzed by the International Nickel Company; the sample came to us through Dr. G. A. Harcourt who was also good enough to exchange notes on some of the critical points in this paper and to confirm the distinction between the two minerals hitherto named rammelsbergite.

In the present account the second author has supplied the observations on polished sections, the first being responsible for the remainder of the work.

RAMMELSBERGITE

HAND SPECIMENS

On freshly broken surfaces rammelsbergite appears tin-white with minute cleavage surfaces revealing a compact, fine-grained, fibrous to bladed texture. On the Schneeberg specimen the rammelsbergite assumes definitely spherulitic forms with interstitial, sharply crystallized quartz; the specimens from Eisleben show some tendency to internal spherulitic arrangement, with veinlets and interstitial areas of calcite. None of the specimens shows isolated crystals or measurable crystal faces.

POLISHED SECTIONS

Rammelsbergite takes a fine polish, appearing smoother and whiter than the other white arsenides of nickel, cobalt and iron when in contact with these minerals. The mineral appears typically in straight-sided blades in random to radiated arrangement. Anisotropism strong; twinning, simple or lamellar, shown by nearly every grain; hardness E, estimated with the steel needle. Etch reactions: HNO_3 , effervesces and etches rapidly to dark brown or black, obscuring the texture; FeCl_3 , etches

quickly to dark brown, bringing out the texture; HgCl_2 , slowly gives a dark brown to iridescent stain which does not rub off; HCl , negative; KCN , negative; KOH , negative. In air saturated with water vapour rammelsbergite is almost completely etched after twelve hours; after one week there is usually some development of white or green bloom.

Eisleben. A section from the specimen used for the analysis (material 3) consists almost wholly of relatively coarsely crystallized rammelsbergite with some interstitial and intergrown calcite (Figs. 1, 2). Impurities, amounting to less than one per cent, are niccolite and a few small inclu-

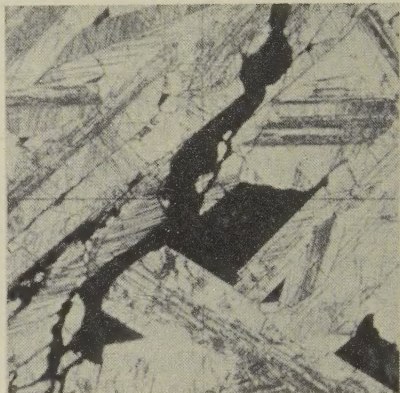
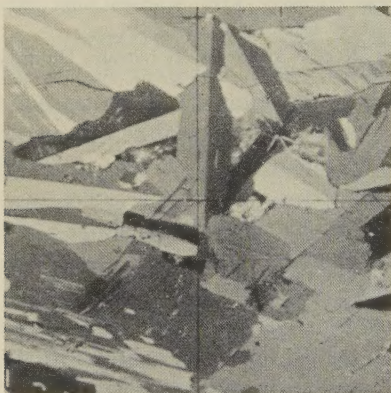


FIG. 1. Rammelsbergite, Eisleben (material 3); interlocking blades showing prominent twinning. Crossed nicols ($\times 67$).

FIG. 2. Rammelsbergite, Eisleben (material 3); interlocking blades and interstitial calcite, etched with FeCl_3 . Plain polarized light ($\times 67$).

sions which appear to be bismuth, argentite and silver. The crystals of rammelsbergite range from straight-sided blades, exceeding 1.0×0.1 mm. in size, to grains as small as 0.02 mm. The well-formed blades make an interlocking to rudely radiated texture. With crossed nicols nearly all the crystals show simple or multiple twinning with straight sharp twin junctions parallel to the elongation. The polarization colours are salmon-pink, russet brown, yellowish brown, yellow, sky-blue, ink-blue, gray, varying somewhat with the orientation of the crystal section. In the elongated (prismatic) sections the ink-blue colour is prominent while the sky-blue colour is commonly shown by the granular (basal) sections.

A section from the specimen which yielded the crystal fragments used for x -ray measurements (material 2) is similar to the foregoing section. The minerals are rammelsbergite with sparse grains of niccolite, small

inclusions of cobaltite, and calcite filling fractures in the ore. The texture is likewise granular to bladed without noticeable radiated arrangement. After one week in wet air the rammelsbergite was completely and deeply etched and partly coated with white bloom.

Schneeberg. The polished section (Figs. 3, 4) shows sheaves of fine-textured, bladed to granular rammelsbergite, with included grains of bismuth (about 1 per cent), bounded by incomplete circular rims (0.4 mm. wide) consisting of loellingite together with a smaller proportion of rammelsbergite and smaltite.¹ The resulting reniform structure shows well

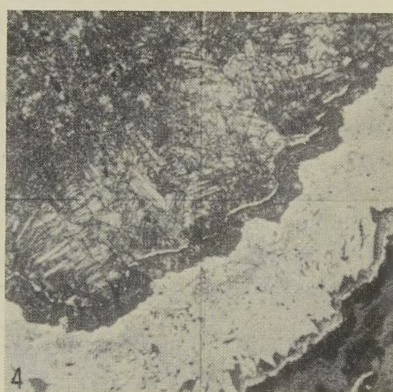
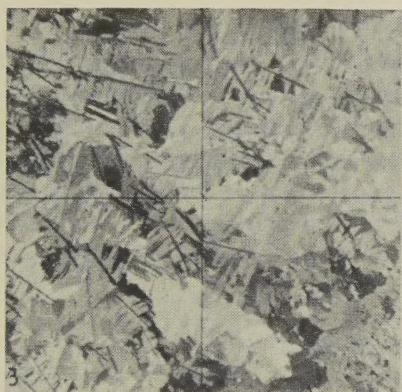


FIG. 3. Rammelsbergite, Schneeberg (material 1); part of a sheaf of bladed rammelsbergite showing complex twinning. Crossed nicols ($\times 67$).

FIG. 4. Rammelsbergite, Schneeberg (material 1); a similar area showing rammelsbergite (dark), with smaltite (white) and loellingite (gray) in the banded rim, etched with FeCl_3 . Plain polarized light ($\times 67$).

under crossed nicols (Fig. 3) and even better after etching with FeCl_3 (Fig. 4), which attacks rammelsbergite without affecting smaltite; loellingite shows only faint differential etching. The polarization colours of the rammelsbergite are dark russet brown, yellowish brown, sky-blue, dark gray. Most of the rammelsbergite shows complex twinning which appears to be a combination of simple twinning on (110) together with lamellar twinning according to an undetermined law. The rim minerals reveal rhythmic precipitation, the complete succession being: smaltite—rammelsbergite—smaltite—loellingite—rammelsbergite—smaltite. Of these, loellingite is the most abundant, forming radially arranged crystals

¹ Smaltite is used in these descriptions to denote zoned cubic arsenides of the skutterudite-smaltite-chloanthite series.

terminating sharply in the outer zone of rammelsbergite. In wet air the rammelsbergite was mostly etched in twelve hours; in a week a green bloom had begun to form in some places.

The Schneeberg rammelsbergite thus shows slight differences as compared with the mineral from Eisleben, namely, lack of the ink-blue polarization colour, more complex twinning, and alteration to a green bloom. In view of the structural identity of the two materials, as shown by x -ray powder photographs, these differences must lie within the range of the properties of rammelsbergite.

SPECIFIC GRAVITY

Table 1 gives some existing measurements of the specific gravity of European rammelsbergite, together with two new measurements obtained with the Berman balance, and the value calculated from the structural cell constants. As compared with the specific gravity calculated from the structural cell, the mostly higher values for Schneeberg are probably due to included bismuth ($G=9.8$) which has been reported in all the analyses and was noted in the polished section; the slightly lower value for Eisleben is due to included calcite.

TABLE 1. RAMMELSBERGITE: SPECIFIC GRAVITY

Locality	Specific Gravity	Observer
Schneeberg	7.129	Breithaupt (1845)
	7.188	Breithaupt (1845)
	7.19	Hilger, in Dana (1892)
	6.9	McCay, in Dana (1892)
	7.23	Peacock (meas.)
Riechelsdorf	7.099	Breithaupt (1845)
	7.14	Linck, in Dürrfeld (1911)
Eisleben	6.97	Peacock (meas.)
	7.05	Peacock (calc.)

CRYSTALLOGRAPHY

Cell dimensions and space group. Crystals fairly suitable for x -ray measurements were obtained from one of the specimens from Eisleben (material 2), by coarsely crushing a fragment with the compact, bladed texture and searching the debris for particles with a distinct long edge made by intersecting cleavage planes. This edge, the direction of elongation of the needles, was taken as the vertical axis, the cleavage being

{110}. Even the smallest crystals secured in this way proved to be twins on (110), with perceptible fibre texture causing some lateral extension of the Weissenberg spots.

On two crystals the following *x*-ray photographs were made with copper radiation: rotation about [001]; Weissenberg photographs of the zero, first and second layers about [001]; Weissenberg photograph about the normal to (110). The films and projections showed orthorhombic symmetry, the observed diffractions conforming to the conditions:

hkl present in all orders
0kl present in all orders
h0l present only with *h+l* even
hk0 present only with *h+k* even

giving the space group $D_{2h}^{12} - Pmnn$, assuming holohedral symmetry.

The cell dimensions of rammelsbergite, with a probable error of 0.01 Å, are given below in comparison with those of marcasite—FeS₂ (Buerger, 1931; 1937 *B*) and loellingite—FeAs₂ (Buerger, 1932).

TABLE 2. RAMMELSBURGITE, MARCASITE, LOELLINGITE:
SPACE GROUPS AND CELL DIMENSIONS

	Rammelsbergite	Marcasite		Loellingite
		1931	1937 <i>B</i>	
Space group	<i>Pmnn</i>	<i>Pmnn</i>	<i>Pmnn</i>	<i>Pmnn</i>
<i>a</i> ₀	3.53 Å	3.37 Å	3.381 Å	2.85 Å
<i>b</i> ₀	4.78	4.44	4.436	5.25
<i>c</i> ₀	5.78	5.39	5.414	5.92

These data bring out a close similarity in the cell constants of rammelsbergite and marcasite, a similarity supported by the cleavage {110} and twinning on (110) which is common to both species. Loellingite, on the other hand, differs substantially from marcasite and rammelsbergite in cell dimensions, cleavage and twinning.² Thus we regard rammelsbergite as closely related to marcasite, rather than to loellingite as suggested by Buerger (1937 *A*, p. 55).

Crystal form, cleavage and twinning. The dimensions of the structural cell of rammelsbergite give the geometrical elements:

$$a_0:b_0:c_0=0.738:1:1.209$$

$$p_0:q_0:r_0=1.637:1.209:1$$

² The lack of agreement between the crystallographic constants of loellingite from Norway (Brögger, 1890, p. 8) and those for loellingite from Franklin, N. J. (Bauer and Berman, 1927; Buerger, 1932) has not yet been explained.

The more widely spaced lattice planes, with indices conforming to the space group conditions, are as follows:

<i>hkl</i>	(011)	(101)	(002)	(110)	(111)	(012)	(020) . . .
<i>d</i>	3.68	3.01	2.89	2.84	2.55	2.47	2.39 Å

From these spacings we would expect the crystals to show {011} as the dominant form and likely cleavage, accompanied by the forms {101}, {002}, . . . The elongation along [001] with cleavage {110} is thus anomalous. On the other hand some crystals of marcasite (Dana, 1892, p. 95, Fig. 2) conform almost perfectly to the above theoretical order of decreasing form importance.

The prism angle of 56°–57°, noted on rammelsbergite by Breithaupt (1845), does not correspond to any simple prism angle in the structural lattice. The elements and forms of Palache and Wood (1904) were derived from crystals doubtfully identified as rammelsbergite. These crystals prove, however, to be maucherite, as shown in a recent description of that mineral (1940). The only other morphological data on rammelsbergite are due to Dürrfeld (1911), whose description of poor crystals from Riechelsdorf is roughly compatible with our crystal lattice. Dürrfeld's elements:

$$a:b:c=0.6798:1:1.1622$$

were obtained from short prismatic crystals formed by {110} (curved faces), with {001}, {011}, {101}.

	DÜRRFELD (measured)	PEACOCK (calculated)
(110):(110)	67°—69°36'	72°53½'
(001):(011)	49 17½	50 24½
(001):(101)	60 25	58 35
	(Schimmermessung)	

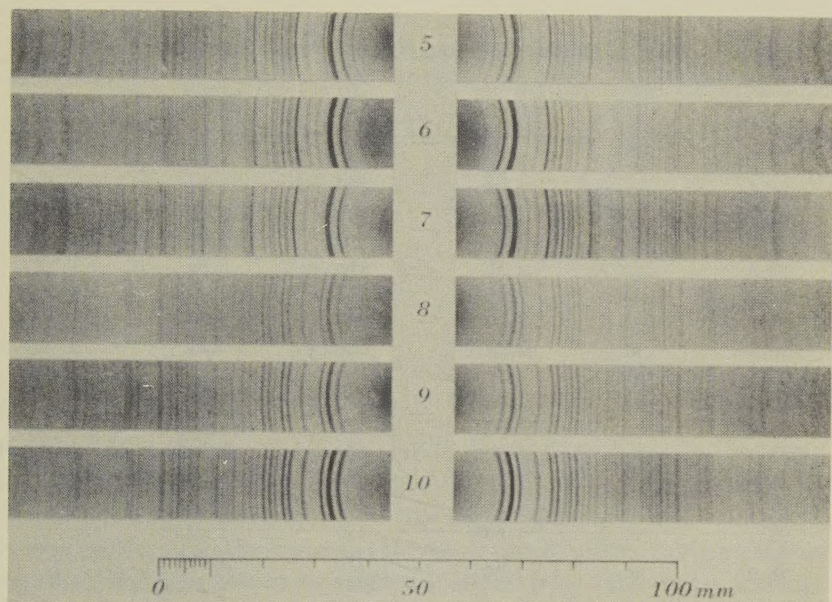
The measured and calculated angles show sufficient resemblance to indicate that the Riechelsdorf crystals are rammelsbergite of vertical prismatic habit.

The cleavage {110}, already known on rammelsbergite, was confirmed by measurement on the fragments used for the x-ray measurements. The twinning on (110) was revealed by all the Weissenberg photographs about [001]. In Friedel's notation this twin law is a case of twinning by reticular pseudo-merohedry with index 3 and obliquity 2°20½'.

POWDER PHOTOGRAPHS

Rammelsbergite and pararammelsbergite are most conveniently and definitely distinguished by means of x-ray powder photographs, which show totally dissimilar patterns for the two minerals (Figs. 5–10). The pattern for Schneeberg (Fig. 5) shows a few lines which are absent in the

identical patterns for Eisleben (Figs. 6, 7); these lines correspond to the strongest lines of bismuth, an observed impurity.



FIGS. 5-10. Rammelsbergite and pararammelsbergite; x -ray powder photographs with unfiltered copper radiation. Camera radius, $360/4\pi$ mm. Exposures, 0.7-1.0 KWH.

FIG. 5. Rammelsbergite, Schneeberg (material 1); the extra lines, as compared with FIGS. 6, 7, are the strong lines of native bismuth.

FIG. 6. Rammelsbergite, Eisleben (material 2); represents the material which gave the single crystal x -ray measurements.

FIG. 7. Rammelsbergite, Eisleben (material 3); represents the material used for analysis.

FIG. 8. Pararammelsbergite, Elk Lake (material 4); represents material used for single crystal x -ray measurements and analysis.

FIG. 9. Pararammelsbergite, Cobalt (material 5a).

FIG. 10. Pararammelsbergite, South Lorrain (material 6).

A full discussion of the powder spectrum of pararammelsbergite has been given by Peacock and Michener (1939); a similar presentation of the powder spectrum of rammelsbergite will be given here to assist in the future recognition of the mineral.³

³ The statement by De Jong (1926) that the cell sides of safflorite and rammelsbergite are the same as those of loellingite is misleading; one of us has likewise obtained the pattern of loellingite from materials labelled "safflorite" and "rammelsbergite"; these appear to be cobalt and nickel bearing varieties of loellingite.

The powder photographs were taken with unfiltered copper radiation, the nickel in the mineral serving almost completely to suppress the β -diffractions. Camera radius $360/4\pi$ mm.

TABLE 3. RAMMELSBERGITE: X-RAY POWDER SPECTRUM

<i>s</i>	<i>I_P</i>	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I_W</i>
12.1 mm.	m	3.68 Å	011	3.68 Å	m
14.2	vw (β)	2.84	110	2.84	m (β)
14.8	vw	3.02	101	3.01	w
15.7	s	2.85	110	2.84	vs
17.5	s	2.56	111	2.55	s
18.2	s	2.47	012	2.47	vs
18.7	vw	2.40	020	2.39	s
20.45	w	2.21	021	2.21	s
21.8	vw (β)	1.875	121	1.872	m (β)
22.4	w	2.02	112	2.03	m
24.3	s	1.871	121	1.872	s
25.4	w	1.796	013	1.787	—
25.9	m	1.763	200	1.765	s
27.1	m	1.690	103	1.691	—
28.1	m	1.635	122	1.633	s
28.9	m	1.593	{ 113 211	{ 1.594 1.592	{ — s
30.2	m	1.530	031	1.536	vs
32.35	s	1.439	212	1.437	vs
34.1	vw	1.373	221	1.379	m
38.5	m	1.236	024	1.237	—
41.7	m	1.157	{ 133 231	{ 1.160 1.159	{ — s
43.35	w	1.121	311	1.121	m
44.6	w	1.096	232	1.095	s
45.9	w	1.071	{ 115 034	{ 1.071 1.070	{ — —
47.0	w	1.052	142	1.054	s
47.9	w	1.037	321	1.038	s
48.7	m	1.024	134	1.024	—
49.5	m	1.011	{ 224 233	{ 1.013 1.008	{ — —
51.1	vw	0.988	240	0.990	m
52.2	w	0.973	241	0.975	m
54.4	w	0.946	330	0.946	m
56.6	w	0.921	{ 150 044 400	{ 0.923 0.921 0.883	{ s — m
61.0	w	0.879	{ 243 152	{ 0.880 0.879	{ — w

TABLE 3 (Continued)

<i>s</i>	<i>I_P</i>	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I_W</i>
62.5	vw	0.867	126	0.866	—
			216	0.833	—
			153	0.832	—
67.5	w	0.832	251	0.832	m
			412	0.831	vs
			045	0.831	—
71.4	vw	0.811	017	0.814	—
			315	0.813	—
			342	0.805	vs
73.2	w	0.803	107	0.804	—
			136	0.803	—
			117	0.793	—
76.5	w	0.791	334	0.792	—
			413	0.791	—

Table 3 represents the Eisleben pattern, giving for each powder ring the half diameter as measured on the film (*s* mm.); the relative intensity of the powder ring by inspection (*I_P*); the planar spacing (*d* meas.) as given by $\theta = s - 0.05$ mm.; the indices of the set or sets of planes contributing to the ring (*hkl*); the planar spacings calculated from the lattice elements obtained from single crystal measurements (*d* calc.); the relative intensity of the Weissenberg spot (*I_W*), if in the range of the Weissenberg photographs taken.

COMPOSITION AND CELL CONTENT

One of the specimens from Eisleben (material 3) provided a sample which was analyzed by the International Nickel Company, giving the values under 1*A* in Table 4. Since the polished section showed very little impurity, apart from the carbonate gangue, the elements other than nickel and arsenic evidently enter into the structure of the rammelsbergite. From the cell volume (97.53 Å³) and the measured specific gravity (6.97) the cell content closely approaches Ni₂As₄ = 2[NiAs₂], with a small amount of cobalt in place of nickel as the only considerable extra constituent. An increase of about 1 per cent in the specific gravity, which is almost certainly on the low side due to intergrown calcite, would give exact agreement with the calculated specific gravity (7.05) of a crystal with the ideal composition Ni₂As₄ (3, Table 4).

The composition of rammelsbergite from Schneeberg is represented by three early analyses, all reporting substantial amounts of bismuth (2.19–5.11 per cent). The best of these analyses (2.4, Table 4) also gives

TABLE 4. RAMMELSBURGITE: ANALYSES AND CELL CONTENTS

	1		2		3	
	A	B	A	B	A	B
Ni	24.58	1.74	26.65	2.15	28.14	2
Co	2.86	0.20	trace	—	—	—
Fe	0.03	0.00	2.06	—	—	—
Cu	0.56	0.04	—	—	—	—
As	70.13	3.90	68.30	3.97	71.86	4
Sb	0.48	0.02	—	—	—	—
Bi	trace	—	2.66	—	—	—
S	0.35	0.05	trace	—	—	—
Gangue	1.45	—	—	—	—	—
	100.44		99.67		100.00	
G	6.97 (meas.)		7.23 (meas.) 7.16 (corrected for Bi)		7.05 (calc.)	

1. Eisleben, Thuringia; *A*—Anal. International Nickel Company; *B*—Atomic content of the structural cell, after deducting gangue.

2. Schneeberg, Saxony; *A*—Anal. Hilger (Dana, 1892, p. 101); *B*—Atomic content of the structural cell, after deducting all Fe as loellingite (7.59 per cent) and all Bi as native bismuth.

3. Ideal composition; *A*—Percentage composition; *B*—Atomic content of the structural cell.

2.06 per cent of iron. Since loellingite and native bismuth were noted in the polished section, a fair estimation of the cell content is obtained by withdrawing Fe as FeAs_2 and Bi as such, and using the specific gravity (7.16) obtained by appropriate correction of the measured value (7.23). The resulting cell content approaches Ni_2As_4 as nearly as we might expect, considering the uncertainties of the case. The excess of Ni over two atoms suggests, but hardly proves, that Ni may partly replace As in rammelsbergite as does Fe in substantial amount in loellingite.⁴

PARARAMMELSBURGITE

SUMMARY OF ESSENTIAL PROPERTIES

The properties of pararammelsbergite are as follows. Orthorhombic (or pseudo-orthorhombic); $a_0:b_0:c_0=0.988:1:1.963$ (from single crystal *x*-ray measurements). Habit, tabular {001}. Forms: $c\{001\}$, $d\{104\}$, $e\{304\}$, $p\{113\}$, $q\{112\}$. Apparent space group, $D_{2h}^{11}-Pbma$ or C_{2v}^5-Pb2a . Cell edges, $a_0=5.74\pm0.01$, $b_0=5.81\pm0.01$, $c_0=11.405\pm0.03$ Å.

⁴ Buerger (1932, p. 167).

Cell content $\text{Ni}_8\text{As}_{16} = 8[\text{NiAs}_2]$. Cleavage $\{001\}$, perfect and easy. Hardness E. Specific gravity 7.12 (meas.), 7.24 (calc.). Hand specimen tin-white, massive, in part minutely crystallized. Polished sections pure white, strongly anisotropic.

The composition is given by the three analyses in Table 5. Analysis 1 represents the material on which the specific data were obtained; analyses 2 and 3 are earlier analyses representing, as nearly as could be ascertained, the materials used for the powder photographs, figures 9, 10, and the polished sections described below. The high cobalt content in analysis 3 suggests that the analyzed sample contained even more smaltite than the specimens described here.

TABLE 5. PARARAMMELSBERGITE ANALYSES

	1	2	3	4
Ni	28.1	27.08	17.46	28.1
Co	0.4	1.94	11.24	—
Cu	none	0.16	—	—
Fe	none	0.56	0.73	—
As	68.5	65.78	66.61	71.9
Sb	—	0.91	—	—
S	2.6	3.05	3.30	—
SiO ₂	—	—	0.84	—
	99.6	99.48	100.18	100.0
G	7.12	7.02	6.73	7.24 (calc.)

1. Moose Horn Mine, Elk Lake, Gowganda, Ontario; anal. Rogers, in Peacock and Michener (1939).

2. Hudson Bay Mine, Cobalt, Ontario; anal. Todd, in Walker and Parsons (1921).

3. Keeley Mine, South Lorrain, Ontario; anal. Rickaby, in Walker (1925).

4. NiAs_2 .

FURTHER OBSERVATIONS ON POLISHED SECTIONS

A further examination of polished sections of pararammelsbergite was made with a view to finding whether this mineral could be distinguished from rammelsbergite without the help of x-ray photographs. The observations given below confirm and supplement the brief descriptions already given in Peacock and Michener (1939).

Pararammelsbergite, like rammelsbergite, takes a fine polish and appears smoother and whiter than the associated white arsenides. The typical crystal shape is rectangular, representing transverse sections of

basal tablets. Anisotropism strong, but not as strong as in rammelsbergite; twinning not observed in typical grains; hardness E, estimated, with the steel needle. Etch reactions: HNO_3 , effervesces and etches rapidly brown to black; FeCl_3 , etches quickly light to dark brown, bringing out the texture; HgCl_2 , slowly gives a brown to iridescent stain which does not rub off; HCl , negative; KCN , negative; KOH , negative. In air saturated with water vapour etching is already perceptible after four hours; in twelve hours the surface is deeply etched; after a week white and green bloom are formed. Pararammelsbergite appears to decompose more rapidly than rammelsbergite in moist air.

Moose Horn Mine, Gowganda. The section consists almost wholly of pararammelsbergite in a mosaic of interlocking grains (0.05 to 0.08 mm.). Crossed nicols reveal no twinning. The polarization colours are russet brown, light brown, yellow, gray; no blue colour was observed. The associated minerals are interstitial niccolite (about 2 per cent) and smaltite (less than 1 per cent) in isolated grains and seams. The pararammelsbergite shows no crystal outlines except in the larger niccolite areas where rectangular outlines appear. These outlines lack the extreme sharpness of the typical blades of rammelsbergite.

Hudson Bay Mine, Cobalt. Sections were made from three different specimens. One of these consists almost entirely of pararammelsbergite with granular texture, passing in places to a rudely radial arrangement of sub-rectangular crystals. The associated minerals are smaltite, cobaltite and gersdorffite (?) which tend to form rims outlining the reniform margin of the main mass of pararammelsbergite. Twinning is not shown. The polarization colours are russet brown, brown, yellow, gray.

A section from another specimen (Fig. 11) shows a marked increase in the amount of cubic minerals (smaltite and cobaltite) which surround roughly elliptical areas (1–8 mm.) consisting largely of typical pararammelsbergite in untwinned, sub-parallel to radial tabular crystals (0.5×0.05 mm.) with the normal polarization colours. Associated with the pararammelsbergite there are some interstitial grains showing the sky-blue polarization and lamellar twinning characteristic of the Schneeberg rammelsbergite. The amount of this mineral is small and its identity with rammelsbergite could not be proved.

In a section from the third specimen, the cubic minerals, together with loellingite, constitute about one-half of the surface. Typical pararammelsbergite with the normal polarization colours occupies the centres of spheroidal areas which are separated by the cubic minerals and loellingite. The outer parts of the spheroidal areas are made up of a mineral with sky-blue polarization and occasional lamellar twinning, which appears to have crystallized after the pararammelsbergite. This mineral

has the appearance of rammelsbergite, but again its identity could not be confirmed.

Keeley Mine, South Lorrain. The section (Fig. 12) shows a reniform structure, the central part consisting of pararammelsbergite while the rim is made up of smaltite and gersdorffite (?). Pararammelsbergite

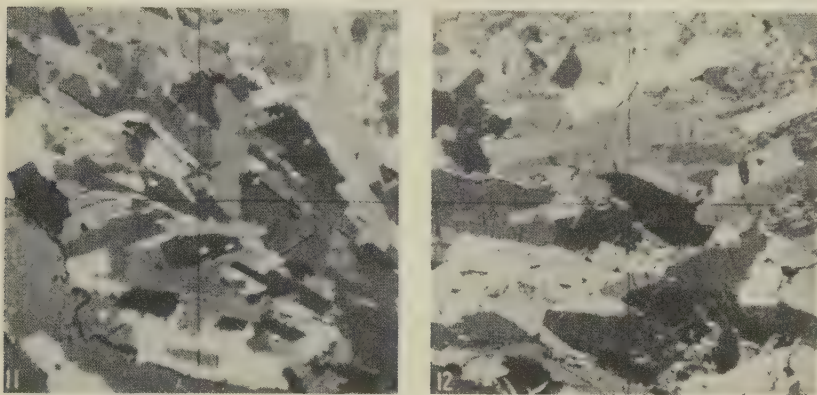


FIG. 11. Pararammelsbergite, Cobalt (material 5 b); untwinned tabular crystals with a few interstitial crystals of rammelsbergite (?) showing lamellar twinning. In the lower left is seen a part of the isotropic rim, enclosing gangue. Crossed nicols ($\times 67$).

FIG. 12. Pararammelsbergite, South Lorrain (material 6); sub-parallel untwinned tabular crystals with an interstitial mosaic of rammelsbergite (?) in the upper right. Crossed nicols ($\times 67$).

forms a granular mosaic passing outward into well formed, diverging, tabular crystals with the normal appearance. As the rim is approached an interstitial mineral appears in increasing amount in a fine grained (0.01–0.02 mm.) mosaic separating the well formed crystals of pararammelsbergite and clearly of later crystallization. This mineral shows slate-blue polarization reminiscent of the Eisleben rammelsbergite. In wet air an abundant green bloom formed on the pararammelsbergite; the mineral resembling Eisleben rammelsbergite etched deeply and turned black but showed no bloom.

Distinguishing characters. From the foregoing it is clear that rammelsbergite and pararammelsbergite have many characters in common; at the same time certain differences have emerged which may serve to distinguish these minerals in polished sections if positive identification by x-ray photographs cannot be made. The distinguishing characters are the following. Rammelsbergite typically forms bladed crystals which are almost invariable twinned; it gives blue polarization colours and is relatively slow to form bloom in a moist atmosphere. Pararammelsbergite

tends to form tabular crystals which are free from twinning; blue polarization colours are not characteristic, and the mineral is relatively prone to the formation of bloom in wet air.

The relation of the mineral resembling rammelsbergite to pararammelsbergite in several of the Canadian specimens indicates that rammelsbergite has the lower temperature of formation and is therefore the more stable modification. But since the identity of the later mineral could not be proved this indication is inconclusive.

THE NATURAL MODIFICATIONS OF NiAs_2

The recognition of pararammelsbergite, as distinct from rammelsbergite and chloanthite, would seem to bring the number of natural modifications of NiAs_2 up to three. However, the existence of a cubic mineral properly represented by the formula NiAs_2 is very doubtful. Chloanthite is commonly intergrown with smaltite, for which the formula CoAs_2 is generally given, in zoned cubic crystals physically very similar to skutterudite, whose composition approaches CoAs_3 . Oftedal (1928) obtained practically identical x -ray measurements from skutterudite and smaltite-chloanthite⁶ and found a structure in terms of CoAs_3 ; the composition CoAs_2 gave an irrational cell content. Although the bulk composition of smaltite-chloanthite commonly lies in the range (Co, Ni)- $\text{As}_{1.5-2.5}$, it would seem that this mineral is structurally the same as skutterudite with extensive and variable replacement of As by (Co, Ni). Furthermore the cell edge of the cubic mineral, $a_0 = 8.19-8.27$, shows no relation to the cell edges of the orthorhombic modifications. Rammelsbergite and pararammelsbergite thus appear to be the only well established natural modifications of nickel diarsenide.

⁶ Recent work in this laboratory has confirmed these measurements.

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WIDTH OF ALBITE-TWINNING LAMELLAE

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ABSTRACT

The width of albite-twinning lamellae depends on the obliquity of the twin. The smaller the obliquity, the higher the frequency of the twin and the thinner the lamellae.

The curve of obliquity *vs.* composition shows that the lamellae should be narrowest in oligoclase, and increase in width, slowly towards anorthite, rapidly towards albite. For pure anorthite, and even more so for pure albite, one should expect the disappearance of polysynthetic twinning and the appearance of single crystals.

These predictions of the French theory of twinning agree with the observations on record.

INTRODUCTION

Probably every petrographer has read the statement that the polysynthetic lamellae of the albite law are broader in calcic than in sodic plagioclases. This, to be sure, is a very intriguing observation. Has it received general acceptance? I do not know, but I am somewhat inclined to doubt it. Few people, at least among my professional friends, seem to make use of it in routine work. Yet, if it were confirmed, it should provide an easy method of obtaining, in a rough way, a general idea of the composition of the plagioclase. Although such a method, admittedly, could never compare in accuracy with any optical determination, it would prove to be a useful and worth-while tool.

In the present paper I shall attempt to answer a two-fold question—is there a theoretical reason why albite-twinning lamellae should be wider in some plagioclases than in others, and are the predictions of the theory substantiated by the observations on record? This question has long haunted me, and I must credit Emmons and Gates' recent challenging article (1939) for giving me the incentive to solve it.

THEORETICAL CONSIDERATIONS

The only theory of twinning truly satisfactory at the present time is that of the French crystallographers. Anticipated in its fundamentals by Haüy himself, originated by Bravais, extended by Mallard, this theory owes its completion and full generalization to G. Friedel (1904, 1933). It is excellently summarized in Friedel's *Leçons* of 1911 and 1926; it is also available, in German, in Niggli's books (1919, 1920).

According to this theory, the fortuitous fact conditioning the occurrence of twins in certain species is the existence, in the space lattice (translation group), of a cell, simple or multiple, endowed, either rigorously or approximately, with more symmetry than the crystal. The lattice having the edges of that cell for its primitive translations, I shall call the *twin lattice*, for convenience. The elements of symmetry (or pseudo-

symmetry) which this particular cell possesses, but which the crystal itself does not have as elements of symmetry, function as *twin elements*. The latter should—and can—always be *reticular*, that is to say, a twin plane is a lattice plane, a twin axis is a lattice row (Law of Mallard). The *index of the twin* is the ratio of the total number of lattice nodes to the number of lattice nodes restored by twinning. The *obliquity of the twin*, in the case of a twin plane, is the angle between the true normal to the twin plane and the lattice row quasi-normal to it. The *twin lattice* extends throughout the twinned edifice, in some cases (obliquity $\neq 0$) with a slight deviation at the composition surface. This prolongation is the condition of stability of the twin. The smaller the index and the obliquity, the more frequent the twin. In particular, for twins having the same index, the smaller the obliquity, the higher the frequency. These conclusions as to frequency are remarkably confirmed by an imposing array of facts.

Let us now turn to the plagioclase problem. It may be conceived, and it is reasonable to suppose, that the width of the polysynthetic lamellae depends on the ease with which twinning can take place. This facility is in direct relation to the frequency of the twin and is likewise an inverse function of index and obliquity. Indeed, in the case of very easy twinning, the prolongation of the *twin lattice* from one twinned individual to the other is nearly perfect and the particles that concur to the building of the crystalline edifice (be they ions, atoms, molecules) will, at every moment during growth, be solicited to adopt either one of two orientations, namely that of the original crystal and that of its twinned symmetrical. Then, since there is not much difference between the two positions from which to choose, it will be, so to speak, easier for the crystal to change its mind, and consequently, the crystal *will* change its mind more often than if the prolongation of the *twin lattice* throughout the dual edifice were less closely approximated. If the obliquity is large, it will be easier for the crystal to continue its homogeneous growth than to shift to its twinned position; the changes of orientation will be less frequent; the lamellae will be wider.

Such considerations are open to the objection that they pay no heed to other than internal factors of crystallization. External factors, such as environment, *Lösungsgenossen*, and thermodynamic conditions in general are disregarded insofar as they do not affect the axial elements (shape of the unit cell). I am confident that, with regard to twinning phenomena especially, the mass of available evidence supports the view that internal factors strongly outweigh external ones. At all events, the above discussion can always be made “fool-proof” by inserting the words “all other things being equal” in front of the second sentence of the foregoing paragraph.

CALCULATIONS

Let $a:b:c$ be the axial ratios and α, β, γ the interaxial angles. If, through the origin, a plane (HKL) is perpendicular to a straight line [UVW], the following relations are known to hold true:

$$(a/H) (aU + bV \cos \gamma + cW \cos \beta) = (b/K) (aU \cos \gamma + bV + cW \cos \alpha) \\ = (c/L) (aU \cos \beta + bV \cos \alpha + cW),$$

in which the indices of the plane and straight lines need not be integers. These equations yield directly the indices ($h'k'l'$) of a plane, not reticular, exactly normal to the twin axis $[uvw]$; the reversed equations will give the indices $[u'v'w']$ of the straight line, not reticular, exactly normal to the reticular plane (hkl) to which $[uvw]$ is quasi-normal. Not all the primed indices are integers.

In the case of albite twinning, $[uvw] = [010]$ and $(hkl) = (010)$. The formulae simplify as follows:

$$\frac{ab \cos \gamma}{h'} = \frac{b^2}{k'} = \frac{bc \cos \alpha}{l'}$$

and

$$\frac{\cos \alpha \cos \beta - \cos \gamma}{ab u'} = \frac{\sin^2 \beta}{b^2 v'} = \frac{\cos \beta \cos \gamma - \cos \alpha}{bc w'}.$$

The obliquity is the angle ϕ between $[uvw]$ and $[u'v'w']$. It is given by the known formula

$$\cos \phi = \sqrt{\frac{\epsilon}{\epsilon'}} \frac{uh + vk + wl}{\epsilon' \sqrt{uh' + vk' + wl'} \sqrt{u'h + v'k + w'l'}},$$

in which

$$\epsilon = \frac{b}{k} (au' \cos \gamma + bv' + cw' \cos \alpha)$$

and

$$\epsilon' = \frac{b}{k'} (au \cos \gamma + bv + cw \cos \alpha).$$

In the present case, the formula reduces to $\cos^2 \phi = \epsilon/v'$.

The data necessary for the calculations are axial elements for plagioclases of known composition. The usual values of the axial elements, given by Dana and Hintze, are tabulated below, together with the composition expressed in *An* percentages.

No.	Plagioclase	$a:b:c$	α	β	γ	% <i>An</i>
I	Albite	0.6335:1:0.5577	94° 3'	116° 29'	88° 9'	2
II	Oligoclase	0.6321:1:0.5524	93° 4'	116° 22½'	90° 4½'	26
III	Andesine	0.6356:1:0.5521	93° 23'	116° 28½'	89° 59'	50
IV	Labradorite	0.6377:1:0.5547	93° 31'	116° 3'	89° 54½'	73
V	Anorthite	0.6347:1:0.5501	93° 13'	115° 55½'	91° 12'	96

The albite data were obtained on material from St. Gotthard. The composition $Ab_{98}An_2$, calculated from a chemical analysis given in Hintze for St. Gotthard albite, is tentatively assigned to the first set of axial elements.

The oligoclase data refer to a specimen from Vesuvius for which a chemical analysis is available. The composition is calculated to be $Ab_{74}An_{26}$. In this calculation, as in the following ones, K_2O is counted in the albite molecule.

The andesine listed comes from Arcuentu. Two chemical analyses, one by Fouqué, the other by Duparc, made on the same material, yield 48.8% An and 51.5% An , respectively. This "andesine" is, in fact, very close to $Ab_{50}An_{50}$.

The axial elements given for labradorite come, partly from Aetna material and partly from Kiev material. The analyses of labradorite specimens from these two localities are very much alike, but they lead to a calculated composition $Ab_{27}An_{73}$, which corresponds to a bytownite rather than a labradorite. This composition must be held in doubt.

Finally, the analysis available for the anorthite material, from Vesuvius, leads to the composition Ab_4An_{96} .

In view of the uncertainty attached to the composition of the albite, other data were sought. Hintze gives axial elements for a number of albite specimens, together with the angle σ which the trace of the pericline twin plane (rhombic section) makes, on the b face, with the edge c . These data are reproduced below.

No.	$a:b:c$	α	β	γ	σ	% An
VI	0.6356 :1:0.5589	94°29'	116°39'	87°28'	34° 6'	1.5
VII	0.6350 :1:0.5586	94°16'	116°43'30"	87°45'20"	31°37'	2.1
VIII	0.63973:1:0.56067	94°12'	116°34'10"	87°48'19"	31°23'50"	2.2
IX	0.63385:1:0.56062	94°15'20"	116°25'43"	87°49'20"	29° 6'	3.0
X	0.63697:1:0.56485	94° 5'33"	116°54'35"	88° 1'54°	28°45'	3.2
XI	0.6358 :1:0.5536	93°56'	116°35'	88°10'	27°47'	3.5
XII	0.63412:1:0.55738	94° 5'22"	116°26'54"	88° 6'45"	27°30'16"	3.6

The composition of these specimens can be tentatively determined from E. Schmidt's curve,¹ which gives the σ angle for the plagioclases. It is realized, of course, that this curve is not very accurate near the sodic end of the series (*cp.* Tom. Barth, 1928), but this is the only method available in this case to estimate the composition. The An percentages given above are read from the curve.

¹ This curve is readily available in Rogers and Kerr, *Thin-Section Mineralogy*, p. 208, McGraw-Hill (1933).

Finally, one good set of elements was given by Lewis (1914), with accompanying chemical analysis:

XIII $a:b:c=0.6335:1:0.5564$, $\alpha=93^{\circ}58'$, $\beta=116^{\circ}21'$, $\gamma=87^{\circ}31\frac{1}{4}'$. The calculated composition is 4.2% *An*.

The *index* of albite twinning is obviously equal to one in all plagioclases. This type of twinning is known as *twinning by pseudo-merohedry*; the unit cell whose pseudo-symmetry determines the twinning (both albite and pericline laws) is known to be *c*-centered, from structural results, but it is easy to see that all nodes are restored by twinning (hence *index*=1).

The values of the indices ($h'k'l'$) of the plane exactly perpendicular to [010] and the indices [$u'v'w'$] of the straight line exactly normal to (010), were computed to seven decimal places by means of a calculating machine, not that the author believed in this fallacious accuracy, but simply as a matter of convenience in working with seven-place tables of natural trigonometric functions. These values are listed here for the purpose of giving an idea of the deviations involved.

No.	h'	k'	l'	u'	v'	w'
I	0.020 4513	1	-0.039 3887	-0.001 2435	0.801 1397	0.100 8263
II	-0.000 8274	1	-0.029 5522	0.039 6696	0.802 6470	0.097 8990
III	0.000 1849	1	-0.032 5827	0.040 9359	0.801 2559	0.106 1743
IV	0.001 0203	1	-0.034 0247	0.039 7325	0.807 1427	0.109 3137
V	-0.013 2921	1	-0.030 8672	0.071 6468	0.808 8612	0.118 6472
VI	0.028 0939	1	-0.043 6887	-0.014 3781	0.798 8127	0.104 3897
VII	0.024 8684	1	-0.041 5591	-0.008 9846	0.797 7621	0.101 6590
VIII	0.024 4989	1	-0.041 0625	-0.008 6563	0.799 9387	0.100 0753
IX	0.024 0864	1	-0.041 6009	-0.007 8465	0.801 9016	0.102 1947
X	0.021 8781	1	-0.040 3116	-0.003 0497	0.795 1660	0.098 8299
XI	0.020 3406	1	-0.037 9746	-0.002 0379	0.799 7446	0.098 0477
XII	0.020 8861	1	-0.039 7488	-0.001 8572	0.801 6273	0.101 6278

The obliquity ϕ was calculated for the thirteen sets of axial elements. The results are tabulated below, together with the plagioclase composition, listed according to increasing anorthite content.

	VI	I	VII	VIII	IX	X	XI	XII	XIII	II	III	IV	V
% <i>An</i>	1.5	2	2.1	2.2	3.0	3.2	3.5	3.6	4.2	26	50	73	96
ϕ	4°31'	4°3'	4°18'	4°13'	4°15'	4°6'	3°57'	4°6'	4°3'	3°28'	3°46'	3°52'	4°20'

DISCUSSION

These results are presented in the form of a graph (Fig. 1), giving the obliquity of the albite twin in terms of plagioclase composition.

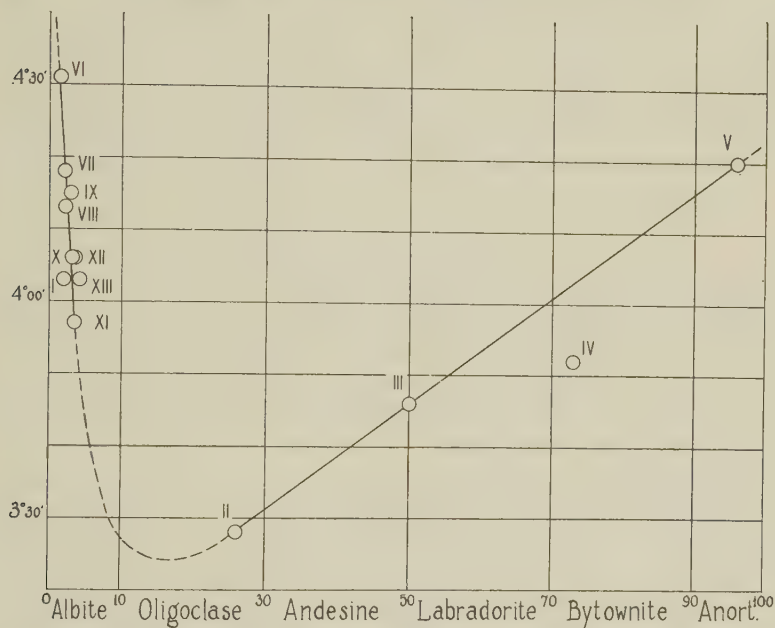


FIG. 1. Albite twin obliquity vs. plagioclase composition. The smaller the obliquity, the more frequent the twin and the thinner the lamellae.

For lack of data the curve cannot be plotted for abscissae ranging from 5% to 25% anorthite content. The points plotted for the albite end of the series are quite satisfactory, with the possible exception of point I, whose reliability was questioned in the preceding section. These points indicate a steep rise of the curve towards pure albite. As to the remaining data, the points II, III, and V, which have been judged most reliable, practically lie on a straight line. The doubtful point IV, if treated as a bytownite, shows an appreciable departure from this curve. It is remarkable, nevertheless, that the value of the obliquity for point IV corresponds to a labradorite composition, about $Ab_{40.4}An_{59.6}$, according to the curve II-III-V. In view of the meagre data available, these results are gratifying; they definitely establish the general trend of the curve for a range of about three-fourths of the plagioclase series, rising steadily from 26% to 96% anorthite.

The only way to fill the gap in the curve is to postulate a minimum somewhere in the oligoclase region. This part of the curve is shown in dash (Fig. 1).

From the above discussion, the predictions of the twinning theory are clear: (1) the albite-twin lamellae should be narrowest in oligoclase; (2) their width should increase as the plagioclase becomes more calcic, the lamellae being widest in anorthites; (3) in the short range from oligoclase to albite, one should expect a rapid widening of the lamellae, to such an extent that for pure or almost pure albite, twinning may cease to be polysynthetic at all.

FACTS OF OBSERVATION

After having presented theoretical predictions, an author is virtually deprived of the right to offer factual observations of his own to substantiate the forecasts. Such *a posteriori* observations could never be free from suspicion. In order to prove (or disprove) my point, I must, therefore, appeal to previous investigators and their observations on record as given in the literature.²

A relevant remark is found in Dufrénoy (1859), who says that anorthite crystals are frequently twinned, but that twinning is "less habitual than for albite and labradorite." Delafosse (1862), describing the polysynthetic repetition of albite twinning, states that "this repetition, however, is fairly rare in albite; it is seen much more frequently in crystals of the next two species,³ oligoclase and labradorite." Des Cloizeaux (1862) furnishes very valuable information concerning the frequency of twinning and the size of the lamellae. His brief remark on andesine ("simple or double twins") is not, of course, very significant.³ His estimation of frequency is as follows: for anorthite, "macles fréquentes"; for labradorite, "macles très-habituellen"; for oligoclase, "macles excessivement fréquentes"; for albite, "macles fréquentes." As to the lamellar character, he makes no special mention of striae or repeated lamellae either for albite or for anorthite; for labradorite, he writes that "lamellar varieties are generally composed of a series of thin strata twinned on g^1 (010) or p (001)"; he describes the Arendal oligoclase crystals as being "apparently single crystals . . . usually traversed by a multitude of thin twinned lamellae joined together parallel to g^1 (010)."

Data on albite are scant. One obvious reason for this is that pure albite is rarely encountered. Fouqué and Michel-Lévy (1879), in their

² Contrary to usual practice and for the sake of clarity, I shall refrain, as much as possible, from quoting in the original language. Crystallographic symbols will be translated as well as words.

³ The validity of andesine was not generally recognized at the time.

discussion of acidic rocks, mention "the extreme abundance of oligoclase and, certainly, the great scarcity of albite." The plagioclase syntheses, which these investigators succeeded in producing, are of special interest. In contrast to synthetic microlites of albite, which were "generally untwinned," it is instructive to read their description of synthetic oligoclase microlites, which showed "very narrow striations," of labradorite microlites, in which they mention "up to twenty twinned lamellae perfectly distinct from one another," and of anorthite microlites "whose twinned lamellae completely resemble natural anorthites, by their arrangement and their great breadth (*grande largeur*)."

Fouqué and Michel-Lévy also provide relevant observations on natural albite ("isolated crystals," "microlites rarely twinned") and natural labradorite ("lamellae often very unequal in size, their thickness exhibiting no regularity"), but their statement on natural anorthite is particularly illuminating: "the lamellae often are of large size, regularly spaced; their appearance is typical enough to permit one to sense anorthite crystals before any measurement of extinction angles and any chemical test."

Further quotations seem well nigh unnecessary. I shall mention two more, which confirm the preceding ones. Tschermak (1897) writes about anorthite: "single crystals are frequent; in repeated twinning, the lamellae are much thicker than in the other plagioclases." A. de Lapparent (1899) remarks that oligoclase shows "twins after the albite law, with numerous striae on p (001)" and that "in thin slices, oligoclase is distinguished by the extreme fineness and regularity of its twinned lamellae"; about anorthite, he states that "its lamellae are wide and fairly well defined."

The consensus seems to be in favor of the theoretical predictions. One discordant note, however, is struck by Luquer (1925) who makes a misleading attempt at generalization when he writes, on the subject of albite twinning in plagioclases, that "the lamellae . . . seem to be broader in the basic than in the acid series." The evidence gathered here shows that exception must be taken to his statement, which is true only in the range extending from oligoclase to anorthite.

CONCLUSIONS

The predictions of the theory are seen to be in excellent agreement with the observations on record.

The width of albite twinning lamellae is in relation to the frequency of the twin. The lamellae are narrowest, and the twinning most frequent, in oligoclase. The universality of finely polysynthetic twinning in oligoclases certainly accounts for the lack of goniometric data on those

plagioclases. The width of the lamellae increases as the plagioclase composition varies from oligoclase to anorthite. In anorthite, the lamellae are broad and twinning is less frequent, as shown by the fact that even single crystals are known. On the sodic end, the same decrease in the frequency of the twin has been noted, many albites having been observed as single crystals. Between sodic oligoclases and calcic albites, with narrow lamellae, on the one hand, and nearly pure albite, found in single crystals, on the other hand, no special mention of albites with broad lamellae has been found in the literature. This is not surprising, in view of the steep slope of the obliquity curve in the albite region. Indeed, it is easy to see (Fig. 1) that only for more than 1.8% and less than 2.3% *An* content can albites be expected to exhibit the same width of lamellae as anorthites. For a more sodic composition, one soon passes into higher obliquities with the consequent disappearance of the polysynthetic character of twinning and even the appearance of single crystals; for a more calcic composition, smaller obliquities demand narrower lamellae, albeit not as thin as those of oligoclase; all of which has been observed.

Finally, it may be remarked that the variations in width of albite-twin lamellae could be presented as strong evidence in favor of the French theory of twinning, were not such additional support wholly superfluous.

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CRISTOBALITE IN BENTONITE

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INTRODUCTION

While examining a bentonite from Casper, Wyoming, in 1934 the author noticed certain lines in the x-ray powder photograph which he was unable to assign to either montmorillonite or any other mineral likely to be associated with it. More recently a sample of bentonite from a locality near Gillette, Wyoming, was received. It is a good example of bentonite since it is uniform in grain size, has a cream color and swells when placed in water. It also contains the unknown mineral which has proved to be cristobalite.

X-RAY EVIDENCE

When the powder of the Gillette bentonite was first x-rayed without any attempt at separation of any of the constituents, it was found to consist of montmorillonite (Table 1) and the then unknown mineral. Unfiltered Fe radiation was used. The precision cameras had an effective radius of 57.3 mm. and the samples were 0.8 mm. in diameter. With this installation it is possible to detect as little as 2 per cent of quartz. None was discovered. Neither was any feldspar or mica detected, which would be more difficult to find in amounts of less than 5 per cent.

An attempt was then made to separate the montmorillonite from the unknown substance by making a colloidal suspension of the montmorillonite in distilled water. This suspension after standing for 24 hours was decanted and then centrifuged for three minutes at 1220 g. Assuming that the density of the cristobalite particles is 2.3 and that of the suspension is close to 1.0, and applying Stokes' law, it follows that all particles larger than 1.25 microns should have been thrown out of suspension. The material still in suspension was recovered by evaporation over a steam radiator and then x-rayed. The film showed good patterns of cristobalite and montmorillonite, but no other lines. It is in no way different from that of the uncentrifuged material. Table 1 shows a comparison of this film with that of cristobalite obtained by devitrifying pyrex glass at 650°C. for 45 days, and with natural cristobalite crystals from Crater Lake, Oregon (Dutton, 3). Also, the lines of montmorillonite obtained from a sample of bentonite from Belle Fourche, South Dakota, are shown for comparison. This montmorillonite was also centrifuged, but it contains no detectable amounts of cristobalite. Since the humidity of the atmosphere makes a difference in the spacing of at least one of the

montmorillonite lines it must be mentioned that the material was x-rayed in a steam heated building with a humidity below 30 per cent.

TABLE 1. X-RAY POWDER PHOTOGRAPHS OF BENTONITE AND CRISTOBALITE
(UNFILTERED Fe RADIATION)

Cristobalite Crater Lake		Devitrified Pyrex		Bentonite Gillette		Montmorillonite Belle Fourche	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
				12.7	10+	12.3	10+
8.873	2	8.993	1				
4.446	5	4.445	3	4.43	5	4.41	2
4.035	10+	4.031	10+	4.031	10		
3.462	1b	3.459	0.5			3.391	0.5
3.126	4	3.126	2b	3.115	2b	3.082	2
2.845	4	2.849	2	2.838	1		
2.746	1	2.737	1	2.721	1		
2.485	4	2.481	3	2.472	3b	2.530	2
2.338	0.5						
2.236	0.5						
2.123	1	2.124	0.5	2.116	1		
2.020	1			2.020	0.5		
1.932	2	1.934	1	1.932	0.5		
1.872	2	1.875	2	1.872	1		
1.734	0.5						
1.694	2	1.698	2	1.686	1	1.681	0.5
1.653	0.5			1.649	0.5	1.637	0.5
1.614	3	1.614	2	1.610	0.5		
1.574	0.5						
1.534	2	1.538	1	1.536	0.5		
1.495	2	1.499	1	1.495	3	1.487	3
1.435	2	1.435	1	1.435	0.5		

b = broad line.

High temperature cristobalite which has been investigated by Wyckoff (4) gives a somewhat different powder photograph from the low temperature modification which has been described by Barth (5). The latter agrees very well with the spacing and intensities given in Table 1.

ABUNDANCE OF CRISTOBALITE

The question remains as to how much cristobalite is present in the Gillette bentonite. A partial analysis by Dr. R. B. Ellestad was made of the material which stayed in suspension after centrifuging. The alkalies were not determined (Table 2) but must be high judging by the defi-

TABLE 2. CHEMICAL ANALYSES

	Bentonite in Suspension, Gillette	Bentonite Natural, Gillette	Average* Montmorillonite
SiO ₂	68.61	68.7	49.16
Al ₂ O ₃	13.07		22.81
Fe ₂ O ₃	2.22**		0.70
FeO			
MgO	2.88		3.48
CaO	0.41		1.64
Na ₂ O	not det.		0.36
K ₂ O	not det.		
TiO ₂	0.09		
MnO			0.04
H ₂ O+	4.19		21.39
H ₂ O—	4.69		
Ignition loss			
Less total H ₂ O	1.30		
Total	97.46		99.58

* Average of seven analyses which are quoted by Mehmel (6).

** Total iron as Fe₂O₃.

ciency of the total percentage. Some sulfate is also present according to Dr. Ellestad.

Assuming that all SiO₂ belongs to the two minerals cristobalite and montmorillonite, it is not difficult to find the percentage of each based on the amount of Al₂O₃ and Fe₂O₃ present. As is well known montmorillonite varies in composition between wide limits. The average computed from five analyses quoted by Mehmel (6, p. 13) is given in the last column of Table 2. If in our analysis about one-half of Fe₂O₃ is added to Al₂O₃ as a constituent of montmorillonite, that is $13.1 + 1.1 = 14.2\%$, and compared with the average montmorillonite, we obtain the proportion $14.2:22.8 = X:100$, in which X is the percentage of montmorillonite in the mixture, $X = 62.3\%$.

Therefore, approximately 37.7 per cent of cristobalite should be present. This is probably somewhat too high on account of the presence of small amounts of other minerals, and perhaps glass. It is thought that 30 per cent cristobalite comes probably closer to the truth. The composition of the uncentrifuged bentonite cannot be very different because an approximate analysis (without hydrofluorization) for SiO₂ shows 68.7 per cent. Also the powder photograph is practically the same as that of the centrifuged portion as mentioned above.

ORIGIN OF CRISTOBALITE

Practically all geologists believe that many bentonitic clays are derived from the decomposition of volcanic ash beds and therefore are associated with eruptions. It is also generally known, due to the work of Fenner (2) and others, that cristobalite has not been synthesized at room temperatures. The lowest temperature recorded by Chrustschoff (1) is 180°–228°C. He claims he obtained it in five hours from amorphous silica in an aqueous solution of hydrofluorboric acid. Fenner (2, p. 358) who made similar experiments at 350°–380°C. did not obtain cristobalite, but quartz. Since Chrustschoff's conditions probably did not closely approach those in nature and low temperature cristobalite is metastable at room temperatures, it may be assumed that it is a mineral of fairly high temperatures. Since this temperature could not have existed in the sediments in which the mineral is found, it must have formed in the outlet of a magma chamber or, in other words, in the throat of a volcano from which it was blown as ash. It is inconceivable that there could have been sufficient heat available for its formation in its journey through the atmosphere.

CONCLUSIONS

Two bentonites from Wyoming contain as much as 30 per cent of cristobalite, even in fractions as fine as 1.25 microns. The place of origin of the cristobalite must be sought in volcanic vents from which the original volcanic ash was derived. Preliminary tests of other bentonites and fuller's earths also indicate the presence of cristobalite.

In conclusion the writer wishes to acknowledge the kind assistance of Dr. R. B. Ellestad and Messrs. Lynn Gardiner and T. E. Gillingham. A grant from the Graduate School of the University of Minnesota has made the investigation possible.

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AN UNUSUAL OCCURRENCE OF GYPSUM AT KALGOORLIE, WESTERN AUSTRALIA

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ABSTRACT

During flooding of several mines at Kalgoorlie, Western Australia, extending over a period of approximately 30 years, certain workings appear to have existed as airlocks, and selenite encrustations have been developed on the walls and roof above the apparent water level in such airlocks. The occurrences are described, also the crystallography and genesis of the gypsum encrustations. From the discussion it appears most probable that the deposits have been developed during a comparatively short period while the mines were being unwatered and pressures in the airlocks decreasing.

INTRODUCTION

In the course of a short visit to the underground workings in the Oroya South Blocks shaft of the Gold Mines of Kalgoorlie property at Kalgoorlie, in January 1939, the writer's attention was drawn to an unusual deposit of gypsum at the No. 11 level of this mine. During flooding, certain parts of this mine appear to have existed as airlocks and the walls and roof of such airlocked chambers (above a well defined water mark) are covered with a layer of coarsely crystalline gypsum.

An exactly similar occurrence was noted during the unwatering of the Paringa Mine at Kalgoorlie in 1934. As there appears to be no record of any similar occurrences, these unusual deposits warrant some record.

DESCRIPTION OF THE OCCURRENCES

(a) *At the No. 11 level (1,096 ft.), Oroya South Blocks shaft, Kalgoorlie.*

The roof and upper parts of the walls of both the east and west crosscuts leading from the shaft are encrusted with well crystallized gypsum, the crust ranging from half an inch to three or four inches in thickness. There is a well defined water mark (emphasized by a coating of ferric oxide) on the walls which apparently indicates the highest level to which standing water could rise as the mine gradually filled with water, after the abandonment of this property about 1910. The cross sections through the shaft and west crosscut (Fig. 2, A and B) show the positions of this water mark and also (Fig. 2, B) the occurrence of the gypsum above the water level. Proceeding westwards from the shaft, where the water level is at the roof of the crosscut, the water line gradually approaches the floor of the workings, because the floor of the tunnel rises gradually from the shaft in that direction (it is the usual practice in mining to drive slightly inclined tunnels to allow drainage to take place into the shaft

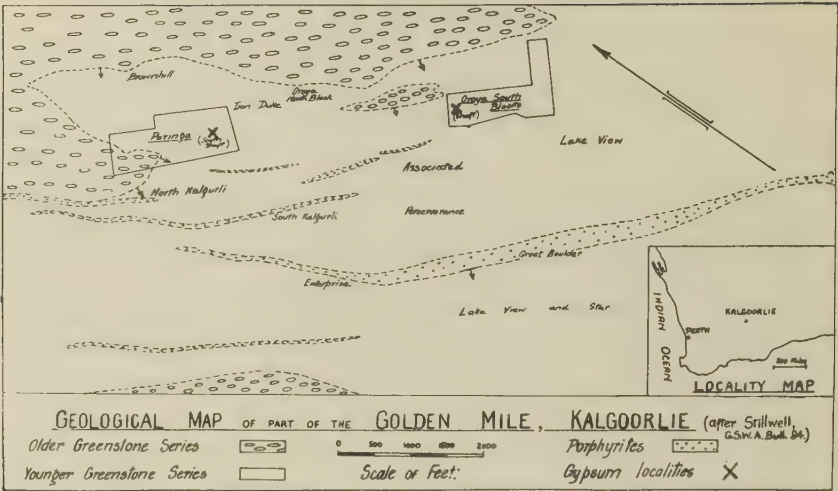


FIG. 1. Geological sketch plan of part of the Golden Mile, Kalgoorlie, Western Australia showing localities where the gypsum deposits occur.

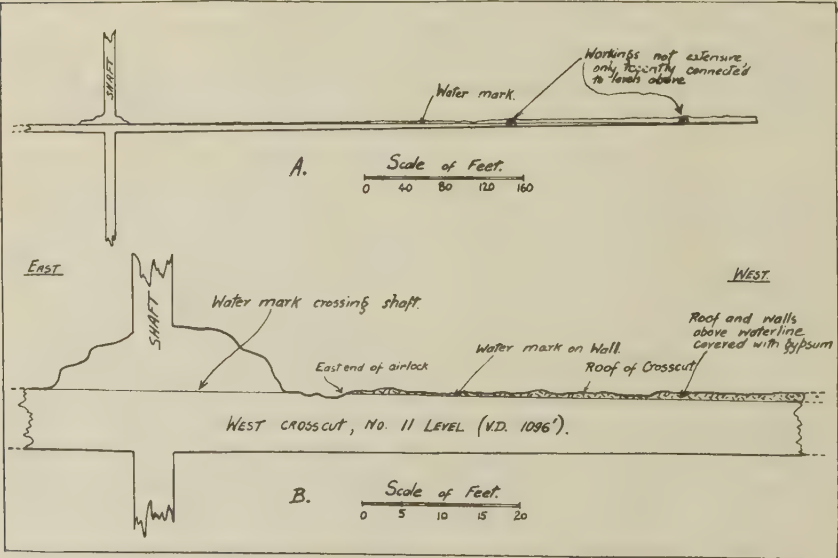


FIG. 2. Vertical sections along the west crosscut, No. 11 level, Oroya South Blocks Mine, Kalgoorlie, Western Australia, showing the development of gypsum above water level.

- A. Total length to show rise of crosscut and "air-lock."
- B. Detail near the shaft (from data supplied by Mr. A. Blatchford).

and to facilitate haulage—the average rising gradient away from the shaft is approximately 1 in 100). It will be apparent that with further rise of water above this level, the part of the tunnel above this water line would remain as an airlock, as the workings at the time of flooding were not connected with the levels above. The only effect of continued flooding of the mine would be to fill up the shaft and the workings at higher levels and to increase gradually the pressure in the airlock and to decrease gradually the volume of the airlock as the water rises. In this particular instance, when unwatering was commenced in 1935, the mine was flooded up to 450 feet from the surface, so that at this time the pressure in the airlock at the 1096 ft. level was the effect of a head of 646 feet of water (i.e., a pressure of approximately 20 atmospheres).

The water line is composite in character, being made up of several lines spread over a width of eleven inches, indicating that the pressure varied from time to time. A less definite iron stained line crosses the shaft at the level of the roof of the crosscut (Fig. 2, B) indicating that the water stood at this level for a considerable period. There is no gypsum on the walls of the shaft.

In the crosscuts (both east and west from the shaft) gypsum occurs in two forms:

(1) As encrustations up to four inches thick on the roof and walls *above the water line*. This is coarsely crystalline material, the crystals averaging $1 \times \frac{1}{2} \times \frac{1}{4}$ inch in size. A noticeable feature is that the crystals are arranged at random, with their long axes pointing in all directions. The thickest deposit is immediately above the water line but the crystals are developed over all the walls and roof above this level.

(2) As a thin irregular coating up to $\frac{1}{8}$ inch thick of minute crystals *below the water line*. This appears to represent a normal evaporation deposit from the water left on the walls after the mine was unwatered. Such thin encrustations are not uncommon in Kalgoorlie mines.

Plate 1 (A) shows the well marked line between (1) above and (2) below the water line.

Details regarding the water levels (which give some indication of the pressures obtaining during the crystallization of (1)) and the period between flooding and unwatering of the mine (which gives some indication of the time during which the crystals may have developed) are:

No. 11 level where the gypsum occurs, 1096 feet vertically below the surface.

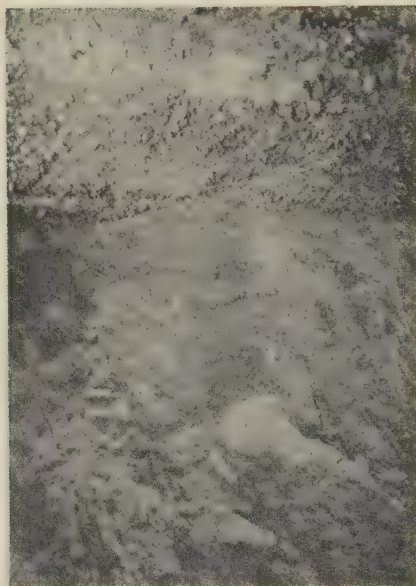
Level of water when unwatering was commenced, 450 feet vertically below the surface.

The crosscuts were driven in 1905, the lower levels were abandoned about 1910 and the upper levels shortly afterwards.

The mine was unwatered in 1935.

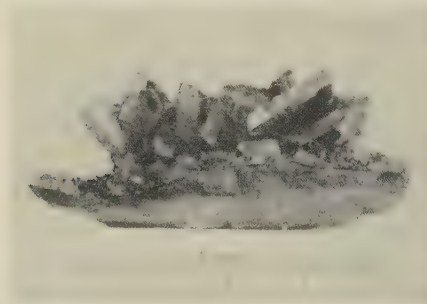
These figures indicate that the "airlock," if such could exist (see dis-

PLATE 1



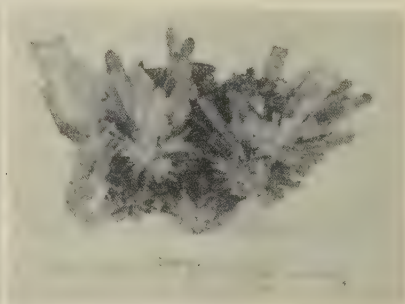
A

A. Photograph of wall of west crosscut, No. 11 level, Oroya South Blocks Mine, showing the profuse growth of gypsum crystals above the water line and their absence below.



B

B. Crystals growing on the wall rock, from the Oroya South Blocks Mine. Showing random orientation of the crystals, development of "swallow tail" twins, striation of the prism and clinopinacoid, central iron stained growth zones within the crystals and the notching of the edge between the prism faces. Several of the larger crystals also show the $\bar{3}02$ cleavage



C

C. Spherulitic growths of gypsum crystals which have developed on the earlier encrustation represented by B (above), from the Oroya South Blocks Mine. Shows "swallow tail" twinning and absence of growth zones and iron staining. The crystals were attached to the earlier growth at the central points of the spherules at the bottom facing the observer.

cussion in next section), has been subject to a pressure of 646 feet of water (approximately 20 atmospheres) for a period of approximately 25 years.

(b) *At the 800 ft. level, South Shaft of the Paringa Mining and Exploration Company's property, Kalgoorlie.*

The occurrence here is similar in all respects to that described above. The gypsum, which is in crystals up to $3\frac{1}{2} \times 1\frac{3}{4} \times \frac{1}{2}$ inches is a clear selenite and has grown with random orientation in an airlock in the top of the tunnel. The features of the occurrence are shown in Fig. 3—all the walls and roof of the drive and crosscuts above the water line are covered with gypsum. The most remarkable feature of this occurrence is that the crystals are developed over the walls and roof of the rises at both the north and south ends of the drive, i.e., in places 11 feet above the water line.

The details regarding the pressure and duration of flooding are:

Level of occurrence: 800 feet vertically below the surface.

Level of water prior to unwatering: 380 feet vertically below the surface.

Approximate date of closing down of the mine: 1901.

Date of unwatering: July, 1934.

The pressure on any airlocks at the 800 ft. level during the period of 33 years while the mine was flooded was therefore due to a head of 420 feet of water (approximately 13 atmospheres).

POSSIBILITY OF EXISTENCE OF AIRLOCKS

Before proceeding to a description of the crystals it is desirable to examine the possibility of existence of airlocks under the high pressures to which the above examples have been subjected. The main factor is the porosity of the country rocks. In both the examples described above, the country rock is a dense fine grained, little sheared, carbonated greenstone which appears to be absolutely impermeable. In the Oroya South Blocks occurrence the existence of an airlock in which the volume has suffered some change (as reflected in the composite water mark) can be demonstrated, but it seems probable that under the 20 atmospheres to which it has been subjected it would be of much smaller volume than is at first apparent.

According to Boyle's law regarding the relation between pressure and the volume of a gas that "the volume occupied by the same sample of any gas at constant temperature is inversely proportional to the pressure," the volume of the airlock at the No. 11 level of the Oroya South Blocks mine would be reduced to approximately one-twentieth of its

original volume (as indicated by the lowest water mark), and that at the 800 ft. level of the Paringa mine to one-thirteenth of its original volume. Unfortunately, owing to a lack of knowledge of the extent of the side workings and stoping in the Oroya South Blocks occurrence the volume of the airlock cannot be calculated. In the Paringa airlock, however, the full volume of the workings is known and it is possible to calculate the volume of the airlock at one atmosphere pressure and so determine the

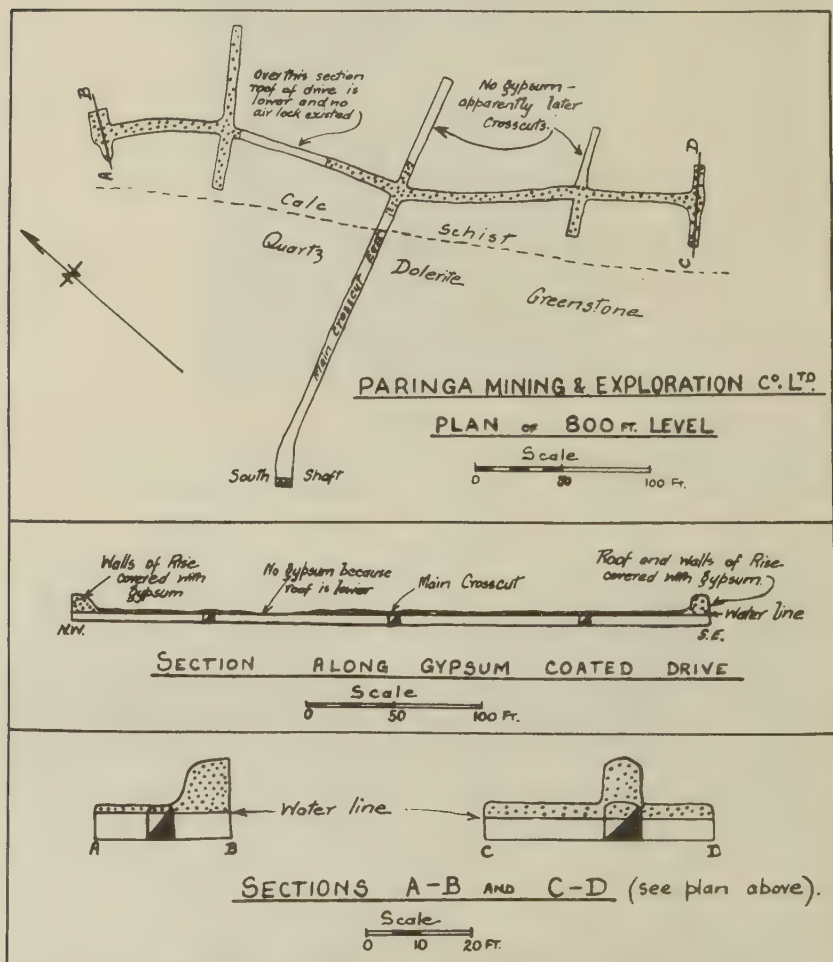


FIG. 3. Plan and sections of the 800 ft. level, South Shaft, Paringa Gold Mine, Kalgoorlie, Western Australia, showing the occurrence of gypsum encrusting walls (dotted) of airlocked workings.

(From data supplied by Dr. C. O. G. Larcombe.)

level at which the water stood when the pressure of 13 atmospheres was effective. Assuming that the average rise of the workings of one foot per hundred holds in this case, the volume of an airlock in these workings at one atmosphere would be approximately 4900 cubic feet. This, when subject to a pressure of 13 atmospheres, would be reduced to approximately 380 cubic feet—barely sufficient to fill the raises at each end of the drives (Fig. 3, sections AB and CD). Although much smaller than would appear from an examination of the water line, there is little doubt that such an airlock has existed.

DESCRIPTION OF THE CRYSTALS

In the thick encrustations in the Oroya South Blocks occurrence there appears to be two distinct growths. The earlier forms crusts up to $2\frac{1}{2}$ inches thick covering the walls, made up of crystals which average 1 inch in length and which are very uniform in habit. They are flattened on (010) and generally elongated parallel to c , although some crystals

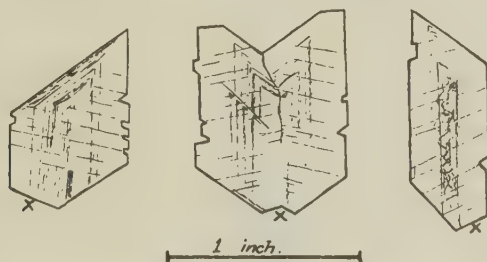


FIG. 4. Section parallel to (010) showing iron stained growth zones, $(\bar{3}02)$ cleavages and notching of the acute angle between the prism faces. The crystals were attached at the points marked x. Crystals from the Oroya South Blocks mine.

are elongated parallel to a . The forms developed are (010), (110), (111) and $(\bar{3}02)$. The (010) and (110) faces are vertically striated and are always the best developed forms. (111) is well developed except on crystals which have grown vertically down from the roof to the water line—here the (111) faces are rounded and etched. The form $(\bar{3}02)$ is always poorly developed, having curved faces, and appears to be best developed on crystals from near the water line, which have suffered considerable etching.

Most of the crystals are twinned on (100) giving the characteristic "swallow tail" twins. Cruciform interpenetration twins are also present.

All of the large twinned crystals show the development of a cleavage parallel to the b -axis, making an angle of 77° with the edge between (110) and $(\bar{1}10)$, and thus having the indices $\bar{3}02$ (Fig. 4). The edge between

the two prism faces is always notched as shown in Fig. 4, these notches being bounded by the faces (111) and $(\bar{3}02)$, or by $(\bar{3}02)$ and (110).

This earlier growth of crystals is invariably iron stained to some extent, especially against the wall rock. The iron stains in the crystals are of interest; generally speaking the crystals show more staining in the parts nearest the wall to which they were attached. Sections cut parallel to the clinopinacoid (Fig. 4) show that the iron staining is arranged in zones, there being often as many as 6 iron stained "ghosts" within a crystal. The forms commonly assumed by these "internal ghosts" are (010), (110) and (111), and they are twinned in the same manner as the enclosing crystal. In most instances the first formed "ghost" crystals were almost as long as the enclosing crystals which have grown by addition of material in the prism zone rather than by growth along the *c*-axis. The cause of the rhythmic growth of the crystals is not apparent, but may be due to changes in pressure within the airlock as the number of periods of growth of the crystals (5 or 6) corresponds to the number of different lines which can be distinguished in the composite water mark (Fig. 5).

A later growth of crystals occurs in places on the surface of the earlier growth described above. In this second "crop" the crystals are arranged in spherulitic aggregates (Plate 1, C) of crystals up to $1\frac{1}{2}$ inches in length. The forms developed on these crystals are (010), (110), (111) and twinning on (100) is common. There is no iron staining in these crystals, they have no $(\bar{3}02)$ cleavage, no notching of the edges between the prism faces and no striations on the (010) and (110) faces.

The crystals from the Paringa mine are all water-clear selenite, though there are occasional crystals having a narrow lath-shaped central zone along *c* which is stained with ferric oxide. The forms developed were (110), (010) and (111). Owing to the absence of marked iron stains in these crystals no information regarding their growth is available.

GENESIS OF THE DEPOSITS

It will be seen then that these crystals have developed in a place that was apparently not accessible to standing water, and also in a closed chamber in which there could be no evaporation. They are, therefore, of interest as they appear to differ in origin from the normal sulphate deposits formed by precipitation from saturated solutions or by evaporation of sulphate-bearing solutions.

The following possible explanations of the origin of these deposits have occurred to the writer:

I. They are deposits formed by evaporation of waters seeping down through the overlying rock before the tunnel was flooded. Such material

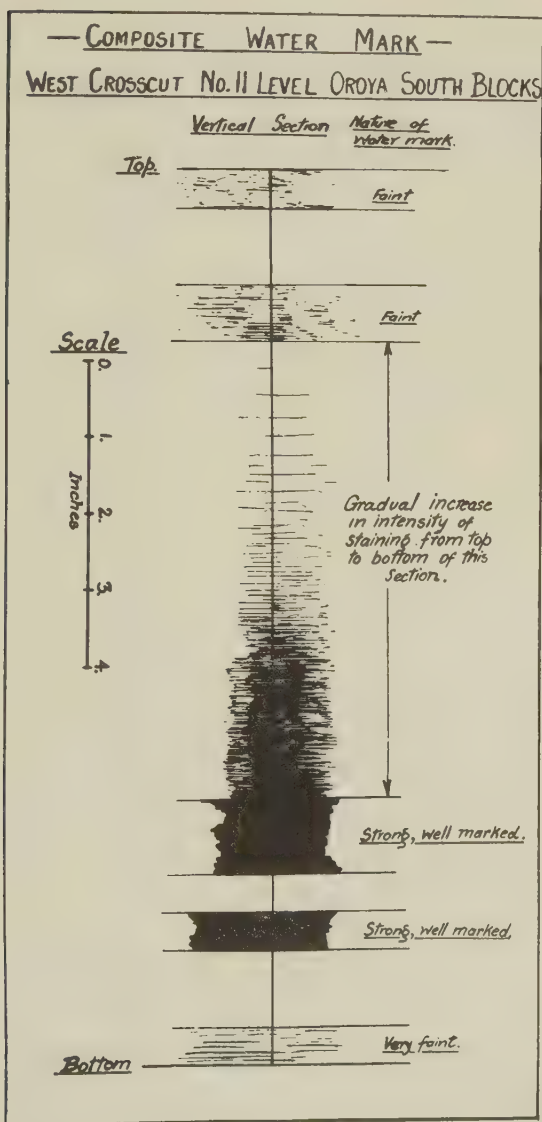


FIG. 5. Detailed section of the composite water line showing the distinguishable water marks due to changes in pressure in the airlock, No. 11 level, Oroya South Blocks mine. (From data supplied by Mr. A. Blatchford.)

would be deposited all over the roof and walls of the tunnel and subsequently be removed by solution up to the water mark as the water gradually rose during flooding of the mine.

The underground water in this area carries a considerable amount of CaSO_4 in solution, as will be seen from the following analysis, which appears to be the best available from this region:

	Parts per cent
CaCO_3	0.0395
FeCO_3	Tr.
CaSO_4	0.1878
MgSO_4	0.3908
MgCl_2	0.5229
NaCl	3.2142
KCl	0.0700
$\text{Al}_2\text{O}_3(\text{Fe}_2\text{O}_3)$	0.0047
SiO_2	0.0009
	<hr/>
Total solids	4.4308

ANALYSIS OF WATER FROM MAINE SHAFT, LAKE VIEW AND BOULDER JUNCTION GOLD MINE, KALGOORLIE, WESTERN AUSTRALIA. (ANALYST: E. S. SIMPSON)¹

Any evaporation of such water would result in the precipitation of CaSO_4 in the form of gypsum. The high concentration of CaSO_4 in some of these underground waters was noted by the writer in 1931 when sections of the main pump column were removed from the shaft of the Croesus mine at Kalgoorlie. The pipe had a diameter of approximately 6 inches, but examination after removal showed that the effective diameter was only about 2 inches as there was a coating several inches thick of crystalline gypsum, consisting of "swallow tail" twinned prisms, growing out normally from the walls of the pipe.

The main arguments against the above theory are:

(1) The possibility of water seeping through these rocks, other than along joints or faults (where the gypsum would be deposited locally) seems remote, because if the rocks were at all permeable the airlock would not be able to exist under the high pressure to which it has been subjected.

(2) If the gypsum were formed in this manner it would be expected that the encrustation would be of uniform thickness all over the walls, but as noted above the growth is most profuse on the walls immediately above the water line.

(3) If such theory were tenable one should expect to find similar

¹ Simpson, E. S., *Geol. Surv. West. Aust., Bull.* **67**, 164, (1916).

occurrences in other workings which have not been flooded. No such occurrences are known in this area.

II. They are deposits formed by reaction of constituents of the atmosphere of the airlock with the wall rocks.

The author has noticed that, when certain mines in this area have been recently unwatered, the atmosphere in the unwatered workings contains considerable amounts of H_2S , probably derived from decomposing organic material left in the workings, or from the alteration of pyrite which is scattered sparsely throughout the country rocks. Here, then, is a constituent of the atmosphere which has possibly played a part in the formation of the gypsum. The source of the lime is not hard to find as in both of the occurrences described the workings are in calc schist (a highly carbonatized "greenstone") which contains a considerable amount of calcite. An analysis of the country rock in the Oroya South Blocks Mine is:

"CHLORITE SCHIST," OROYA SOUTH BLOCKS MINE, KALGOORLIE, WESTERN AUSTRALIA.

Analyst: C. G. Gibson.²

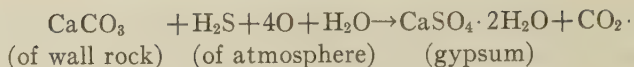
SiO_2	40.61
Al_2O_3	8.85
Fe_2O_3	—
FeO	12.42
MnO	0.21
MgO	4.50
CaO	14.27
Na_2O	0.84
K_2O	3.17
$\text{H}_2\text{O}-$	0.10
$\text{H}_2\text{O}+$	2.30
TiO_2	0.15
CO_2	12.75
FeS_2	0.29
	<hr/>
	100.91

The development of gypsum by reaction of sulphuric acid solutions with calcite-bearing rocks is well known.³ Wilder considers that many gypsum deposits may have been formed by the action of sulphurous vapours on limestone.⁴ It is conceivable, therefore, that in the present instance the gypsum may have developed through oxidation of H_2S in the damp atmosphere of the airlock to H_2SO_4 which would be deposited on the walls and then react with the calcite of the wall rocks to give gypsum, thus:

² Simpson, E. S., *Geol. Surv. West. Aust., Bull.* **67**, 74, (1916).

³ Stone, R. W., *U. S. G. S., Bull.* **697**, 25, (1920).

⁴ Wilder, F. A., *Bull. Geol. Soc. Am.*, **32**, 391, (1921).



If this process operated there would not be sufficient oxygen in such a closed space to produce the quantity of gypsum observed. If we consider the walls and roof of a chamber 400 ft. \times 5 ft. \times 4 ft. to be covered by an encrustation of gypsum half an inch thick, then the total weight of gypsum is approximately 21,000 pounds, whereas in this space there is only 75 pounds of oxygen available for oxidation processes, so it is clear that the above hypothesis is inadequate.

Pyrite is a constituent of the wall rocks and oxidation of this mineral above the water level would give rise to a sulphuric acid solution, covering the walls, which would react with the calcite to produce gypsum. In the Paringa occurrence there is an abundance of pyrite available as the workings are in lodestuff (highly pyritized calc schist), but it is doubtful whether in the Oroya South Blocks occurrence sufficient pyrite was available. In any case, the objections regarding an insufficiency of oxygen as noted above also holds in this instance.

III. They are deposits from solutions which have wetted the walls above the water level, crystallization being caused by a lowering of pressure.

The walls of the chamber would be kept wet by condensation from the saturated atmosphere, and over a long period of time it is likely that calcium sulphate from the standing water might diffuse through this thin layer. If this were the case, one should expect that the thicker deposits would be developed just above the water line where the supply of CaSO_4 would be more quickly renewed—this agrees with the observed distribution of the gypsum encrustation which is thicker just above the water line than in the higher parts of the tunnel. In addition the CaSO_4 content of the solution wetting the walls may be increased by the reaction of H_2S in the atmosphere with the wall rock as described under II above.

It would appear possible then to have a CaSO_4 solution developed on the walls but the question of the precipitation of the CaSO_4 is more difficult. We are dealing here with a closed system in which evaporation can not take place once the atmosphere becomes saturated. There are two possible factors which may have caused precipitation:

A. *Temperature changes.*

The solubility of CaSO_4 varies with the temperature. According to Hulett and Allen⁵ the solubility of gypsum in water increases up to a

⁵ Hulett, G. E., and Allen, L. E., *Jour. Am. Chem. Soc.*, **24**, 674, (1902).

maximum at 40°C. and with further rise of temperature the solubility decreases. The figures quoted for saturated solutions of gypsum in water at various temperatures are:

At 0°C. saturated solutions contain	0.17590 gm. CaSO_4 per 100 cc. soln.
30°C.	0.20905
35°C.	0.20960
40°C.	0.20970 (max.)
45°C.	0.20835
55°C.	0.20090
75°C.	0.18475
100°C.	0.16190

Small temperature changes would, therefore, tend to bring about changes in the equilibrium of saturated solutions; below 40°C. any lowering of temperature would tend to produce precipitation, and above 40°C. any rise in temperature would produce a like result. Ground temperature changes need not be further considered here as a cause of the gypsum deposits since we have no reason to think that they have occurred in the last 40 years.

B. Pressure changes.

There are very few data available regarding the solubility of CaSO_4 in water at various pressures. Comey and Hahn⁶ give the following:

100 gms. saturated CaSO_4 solution at 1 atmosphere and 15°C. contain 0.206 gm. CaSO_4 .

100 gms. saturated CaSO_4 solution at 20 atmospheres and 15°C. contain 0.227 gm. CaSO_4 .

Gibson⁷ says that the increase in solubility of gypsum per 1000 bars increase in pressure is 57%.

From these figures it appears that the precipitation from saturated CaSO_4 solutions could only be effected by a decrease in pressure.

In the occurrence of gypsum from the Oroya South Blocks mine at Kalgoorlie there is a close relation between the number of growth zones in the crystals (Fig. 4) and the number of distinguishable marks in the composite water line (Fig. 5), which appears to indicate the close relation between precipitation and pressure changes. The figures quoted above indicate that precipitation is more likely to be brought about by lowering of the pressure, and it would appear most probable that the greater part of the gypsum in these airlocks was deposited during the period when the mine was being unwatered and the pressure in the airlock was being

⁶ Comey, A. M., and Hahn, D. A., *A Dictionary of Chemical Solubilities* (2nd. Edition), New York, 1921, p. 946.

⁷ Gibson, R. E., On the effect of pressure on the solubility of solids in liquids: *Am. Jour. Sci.*, **35A**, 65, (1938).

reduced. Some, however, may have been developed previously owing to changes in the water level by intermittent working in neighbouring mines, because changes in the water level of these mines would undoubtedly affect the water level in the Oroya South Blocks.

The selenite crystals of the Paringa mine, although they show no growth zones, may have developed in a similar fashion.

IV. They are deposits from solutions which have wetted the walls, crystallization taking place under conditions of falling pressure and by evaporation.

The possibility of the existence of airlocks in these flooded mines has been discussed above—it has been shown that under the high pressures to which such airlocks have been subjected, they would be reduced to very small dimensions. Consequent upon the reduction of pressure during unwatering operations the airlock would expand and evaporation would be possible into the larger space available. The sequence of events in the formation of the gypsum deposits in these airlocks seems to be:

(1) Flooding of the mine giving rise to an airlock which was gradually reduced to a very small volume. This airlock has persisted for a number of years and the ground water (under high pressure) has become heavily charged with CaSO_4 . There is no reason for any crystallization of gypsum during this period because the pressure (and therefore the solubility of gypsum) was increasing and also because no evaporation could take place.

(2) Unwatering of the mine causing a decrease in the pressure and consequent increase in volume of the airlock, the walls of which would be wet with CaSO_4 -saturated solution. With relief of pressure the CaSO_4 will begin to crystallize and this crystallization will be assisted by evaporation from the walls into the larger airspace now available.

In the Oroya South Blocks there were probably a number of causes in the sinking of the water level as unwatering proceeded due to extensive workings (including large stopes) at various levels which had to be emptied before the pressure at that stage was effectively reduced. This would give rise to the distinct water marks which have been correlated with the growth zones in the crystals. In the Paringa mine, unwatering took place uniformly and comparatively rapidly (because of the limited extent of the workings and the absence of large stopes) so that the crystals have grown uniformly and have not, at successive stages of their growth, been covered with iron oxide films.

CONCLUSION

It appears, from the above discussion, that the hypothesis described under IV is most probable and this indicates that the gypsum crystals

were formed in a very short period (of several months) while the mine was being unwatered and not during the longer period when the mine was flooded.

GYPSUM OCCURRENCES IN NATURAL CAVITIES

A natural cavity in quartz dolerite greenstone, filled with gypsum, occurred at the 700 ft. level in the Main shaft workings of the South Kalgurli Gold Mine at Kalgoorlie, and is of interest in connection with the above occurrences in artificial openings. The original cavity was somewhat irregular in shape measuring 15 ft. \times 8 ft. \times 3 ft. thick and was filled with clear selenite from which cleavage fragments up to several feet long could be obtained. It would appear to be very similar in origin to the occurrences described above and may have developed comparatively recently when mining operations brought about a lowering of the water table and led to a decrease in pressure on the solutions in this cavity

An interesting occurrence of gypsum in a natural cavity has been described by Jutson⁸ from the Sand Queen mine at Comet Vale, Western Australia. The cavity was a transverse, nearly vertical opening in the main reef and was traceable downwards for several hundred feet. This "vugh" was filled with calcite and selenite from which large cleavage fragments were obtainable. This again appears to be a deposit which could have been formed in the manner outlined above.

ACKNOWLEDGMENTS

The writer wishes to acknowledge his indebtedness to Mr. A. Blatchford who drew his attention to the Oroya South Blocks gypsum encrustations and who supplied data regarding this deposit. Also to Dr. C. O. G. Larcombe and Mr. A. W. Winzar for information regarding the Paringa occurrence and to Professors E. de C. Clarke and N. S. Bayliss for discussion during the preparation of this paper.

⁸ Jutson, J. T., *Geol. Surv. West. Aust., Bull.* **79**, 21, (1921).

CRYSTALLOGRAPHY OF DOLEROPHANITE

W. E. RICHMOND AND C. W. WOLFE,
Harvard University, Cambridge, Mass.

Crystals of dolerophanite, Cu_2SO_5 , formed during the eruption of Mt. Vesuvius in October 1868, were described by Scacchi (1873). V. Goldschmidt (1886) chose a different orientation from that of Scacchi and calculated new elements. Dana (1892) adopted Scacchi's elements, but interchanged the *a*- and *c*-axes. Strandmark (1902), working with artificial crystals found in copper slag, selected a still different orientation; and Zambonini (1935), in an exhaustive study of the morphology, adopted Strandmark's orientation but calculated new elements based on more reliable measurements.

TABLE 1. DOLEROPHANITE: CORRELATION OF SETTINGS

Forms	Scacchi	Goldschmidt	Dana (1892)	Strandmark-Zambonini
<i>a</i> 100	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>
<i>b</i> 010	<i>C</i>	<i>C</i>	<i>b</i>	<i>C</i>
<i>c</i> 001	<i>A</i>	<i>A</i>	<i>a</i>	<i>A</i>
<i>m</i> 110	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
<i>o</i> 410	—	—	—	<i>o</i>
ω 011	—	—	—	ω
<i>l</i> 201	—	—	—	<i>l</i>
μ 304	—	—	—	<i>u</i>
<i>j</i> 405	—	—	—	<i>j</i>
<i>d</i> 101	<i>d</i>	<i>d</i>	<i>d</i>	<i>J</i>
<i>B</i> 403	<i>B</i>	<i>B</i>	<i>C</i>	<i>B</i>
<i>e</i> 201	<i>e</i>	<i>e</i>	<i>e</i>	?
<i>f</i> 401	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
<i>v</i> 111	—	—	—	<i>v</i>
<i>r</i> 112	<i>r</i>	<i>r</i>	<i>r</i>	<i>r</i>
<i>p</i> 314	<i>p</i>	<i>p</i>	<i>p</i>	<i>p</i>
<i>n</i> 133	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>
<i>s</i> 111	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
<i>q</i> 312	<i>q</i>	<i>q</i>	<i>q</i>	<i>q</i>
<i>h</i> 803	—	<i>h</i>	—	<i>h</i>
<i>y</i> 601	—	—	—	<i>y</i>

An x -ray crystallographic study shows that the orientation and unit of Goldschmidt correspond with the face-centered lattice generally chosen by x -ray crystallographers, and the orientation of Strandmark is the corresponding body-centered lattice of the same network. The transformations of other orientations to the Goldschmidt orientation and unit are:

Scacchi to Goldschmidt	$-\bar{4}00/040/303$
Dana to Goldschmidt	$-00\bar{4}/040/303$
Strandmark to Goldschmidt	$\bar{1}0\bar{1}/0\bar{1}0/001$

The correlation of forms is given in Table 1. The letters used here are those of Scacchi except that the pinacoids and unit prism have been given letters conforming to standard usage.

The accepted forms of dolerophanite are shown on the gnomonic projection (Fig. 1). A typical crystal is illustrated in Fig. 2.

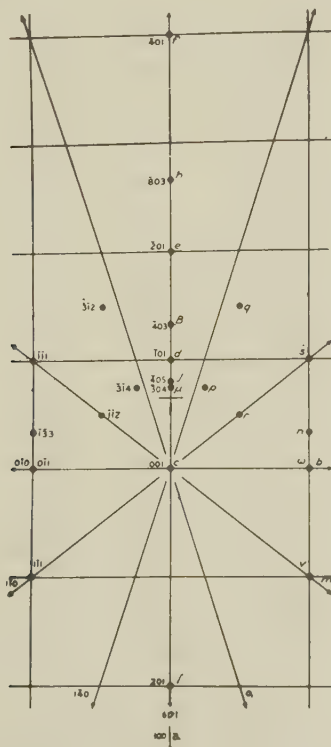


FIG. 1. Gnomonic projection of the accepted forms of dolerophanite.

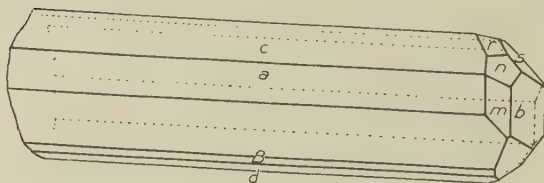


FIG. 2. Typical crystal of dolerophanite.

Since Zambonini's measurements are probably the best, his elements, transformed to Goldschmidt's orientation are adopted in the angle table (Table 2).

TABLE 2. ANGLE TABLE OF DOLEROPHANITE, Cu_2SO_5
Monoclinic; prismatic— $2/m$

$$a:b:c=1.4842:1:1.2089; \beta=122^\circ 18\frac{1}{2}'; p_0:q_0:r_0=0.8145:1.0217:1$$

$$r_2:p_2:q_2=0.9787:0.8127:1; \mu=57^\circ 41\frac{1}{2}'; p'_0=0.9637, q'_0=1.2089, x'_0=0.6324$$

Forms	ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
<i>c</i> 001	90° 00'	32° 18½'	57° 41½'	90° 00'	0° 00'	57° 41½'
<i>b</i> 010	0 00	90 00	—	0 00	90 00	90 00
<i>a</i> 100	90 00	90 00	0 00	90 00	57 41½	0 00
<i>m</i> 110	38 33½	90 00	0 00	38 33½	70 32½	51 26½
<i>o</i> 410	72 35½	90 00	0 00	72 35½	59 20	17 24½
ω 011	27 37	53 45½	57 41½	44 23	45 37	68 03
μ 304	—90 00	5 13½	95 13½—	90 00	37 32	95 13½
<i>j</i> 405	—90 00	7 53½	97 53½	90 00	40 12	97 53½
<i>d</i> 101	—90 00	18 20	108 20	90 00	50 38½	108 20
<i>B</i> 403	—90 00	33 07½	123 07½	90 00	65 26	123 07½
<i>l</i> 201	90 00	68 39½	21 20½	90 00	36 21½	21 20½
<i>e</i> 201	—90 00	52 19½	142 19½	90 00	84 38	142 19½
<i>h</i> 803	—90 00	62 42	152 42	90 00	95 00½	152 42
<i>f</i> 401	—90 00	72 45½	162 45½	90 00	105 04	162 45½
<i>y</i> 601	90 00	81 08½	8 51½	90 00	48 50	8 51½
<i>r</i> 112	13 59	31 55	81 26½	59 08	38 13	82 39½
<i>v</i> 111	52 51½	63 27½	32 04	57 18½	40 38½	44 30½
<i>s</i> 111	—15 19½	51 25	108 20	41 04	65 22½	101 55½
<i>r</i> 133	14 26	51 18	72 43	40 54	50 46½	78 47
<i>p</i> 314	—16 49½	17 31½	95 13½	73 15	40 35½	95 00
<i>q</i> 312	—53 22½	45 22½	129 07	64 52½	73 14	124 50

Uncertain forms: 10.0.1, 13.0.1, 14.0.1, 883, 269.

X-RAY STUDY

Richmond (1939) determined the lattice constants of dolerophanite. The crystal used for this work was approximately 0.5 millimeter in length and 0.25 millimeter in section. Rotation and Weissenberg photographs were taken about the $b[010]$ and $c[001]$ axes, using copper radiation.

Reciprocal lattice projections were made of the zero and first layer-line photographs taken about the $b[010]$ axis.

The reciprocal lattice chosen to conform to morphological conventions resulted in a body-centered lattice. The alternate face-centered lattice was therefore adopted. The reflections on the Weissenberg photographs, referred to this lattice, are:

$$\begin{aligned}(hkl) &= \text{with } h \text{ and } k \text{ even} \\ (h0l) &= \text{with } h \text{ even} \\ (0k0) &= \text{with } k \text{ even}\end{aligned}$$

These criteria, together with the fact that previous morphological investigations indicated holohedral symmetry, give the space group $C_{2h}^3 - C2/m$.

The lattice constants, calculated from the Weissenberg photographs are:

$$\begin{aligned}a_0 &= 9.39 \text{ \AA} \\ b_0 &= 6.30 \text{ \AA} \\ c_0 &= 7.62 \text{ \AA}\end{aligned} \quad a_0:b_0:c_0 = 1.490:1:1.209; \beta = 122^\circ 41\frac{1}{2}'$$

Contents of the unit cell. The analysis by Zambonini and a new specific gravity (4.17) determined by Richmond, together with the lattice constants, give the content of the unit cell as shown in Table 3.

TABLE 3. DOLEROPHANITE: CONTENTS OF THE UNIT CELL

	1	2	3		4	5	6
CuO	65.20	66.06	0.830	Cu	0.830	7.98	8
SO ₃	33.49	33.94	0.424	S	0.424	4.07	4
Insol.	1.31	—	—	O	2.120	20.20	20
	100.00	100.00					

1. Analysis of dolerophanite; analyst, Zambonini.
2. Analysis recalculated to 100%.
3. Molecular proportions.
4. Atomic proportions.
5. Number of atoms in the unit cell.
6. Theoretical number of atoms in the unit cell.

From column 6 the unit cell contains $4[\text{Cu}_2\text{SO}_5]$.

OPTICAL PROPERTIES

Zambonini gave incomplete optical data. Therefore, Dr. Harry Berman determined the indices of refraction and optical orientation of dolerophanite which, in Goldschmidt's orientation, are:

		Indices (Na)	
X	deep brown	1.715	positive
$Y=b$	brownish yellow	1.820	$2V=85^\circ$
$Z/\wedge c = -10^\circ$	lemon yellow	1.880	$r > v$, very strong, crossed dispersion

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CUPROBISMUTITE—A MIXTURE

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Examination of the type specimen of cuprobismutite upon which Hillebrand founded the species was made possible by the loan of the specimen (U.S.N.M. 92902) by the U. S. National Museum. This examination revealed the definite occurrence in it of two minerals, bismuthinite and emplectite, both in measurable crystals. Since a mixture of these substances would give the composition revealed by Hillebrand's analysis, the species has no validity. But, since both of the above-named minerals are so rare in measurable crystals, data observed are here recorded.

Cuprobismutite was given species rank by Dana in the *System*, p. 110, on the basis of Hillebrand's analyses, although the physical description was very incomplete. It was discredited by Short (1931), who examined the type specimen minerographically and identified the mineral present as emplectite. This conclusion, however, has not been accepted by Schneiderhöhn and Ramdohr, nor by Gaudin and Dicke (1939), but none of these authors gives data which in the least establish the species.

The type specimen from the Missouri Mine, Hall's Valley, Park County, Colorado, is a small mass of siliceous ore, dark from the embedded needles of emplectite which it contains. In drusy openings in the quartz the metallic minerals have formed free crystals. The most abundant of these are iridescent tarnished thin plates and needles which proved to be emplectite. Thicker striated crystals in two or three cavities proved to be bismuthinite. Chalcopyrite crystals and grains are rare. Nothing was seen that could be identified with the wolframite found to be present in the ore by Hillebrand.

Emplectite. The thin plates are numerous and generally extend from wall to wall of the cavities in which they occur. Broken surfaces show the perfect cleavage parallel to (010) and also the less perfect (001) cleavage. The plates are deeply striated vertically so that they give an endless chain of colored signals. They seem to be flattened, not parallel to the pinacoid (010) but to a pair of prism planes, not exactly measurable. The narrow edges of the plates revealed minute faces of the forms shown in Table 1 and in the figure. Comparison of the measured and calculated angles in Table 1 leaves no doubt of the identity of these crystals with emplectite as recently described by Palache and Peacock (1933).*

* Since the publication of this paper the setting has been transformed to correspond to the structure cell. Transformation formula Palache and Peacock to new position 010/300/001. The letters as given above are the same as used in the published table. The new ϕ is $(90^\circ - \phi)$ of that table.

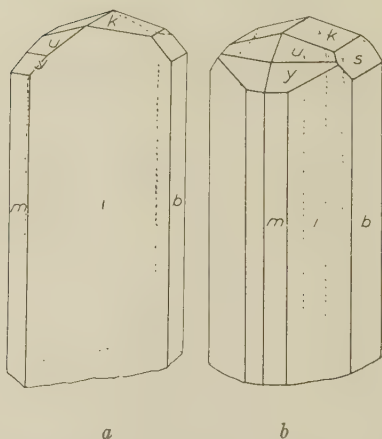


FIG. 1a. Emplectite. Distorted crystal flattened parallel to a pair of prism planes.

FIG. 1b. The same crystal restored to symmetrical development.

TABLE 1. MEASUREMENTS OF EMPECTITE

Forms	No. of faces	Measured		Calculated	
		ϕ	ρ	ϕ	ρ
<i>k</i> 011	2	0°00'	15°00'	0°00'	15°06'
<i>s</i> 051	2	0 00	53 12	0 00	53 27
<i>h</i> 201	1	90 08	51 30	90 00	51 57
<i>u</i> 111	2	67 07	34 47	67 06½	34 44½
<i>y</i> 221	2	67 07	54 00	67 06½	54 12½
<i>p</i> 131	1	38 10	45 37	38 17½	45 52½



FIG. 2. Crystal of bismuthinite.

Bismuthinite. In a few cavities, besides the plates of emplectite, there were somewhat stouter reddish crystals, two of which were measured. They gave measurements which agree well with the angles of bismuthinite as given by Peacock (1933).**

TABLE 2. MEASUREMENTS OF BISMUTHINITE

Forms	No. of faces	Measured		Calculated	
		ϕ	ρ	ϕ	ρ
<i>q</i> 130	2	18° 58'	90° 00'	18° 40½'	90° 00'
<i>o</i> 120	1	26 51	90 00	26 53	90 00
<i>m</i> 110	1	45 26	90 00	45 24	90 00
<i>n</i> 210	1	63 47	90 00	63 45	90 00
<i>N</i> 021	2	0 00	34 44	0 00	34 58½
<i>z</i> 301	1	90 00	46 56	90 00	46 46½
<i>S</i> 111	2	45 01	26 36½	45 24	26 28½
α 221	3	45 41	45 00	45 24	44 53½
<i>w</i> 121	3	27 18	38 01	26 53	38 06½
σ 211	1	63 40	38 54	63 45	38 20½

Figure 2 shows the forms present in somewhat idealized proportions.

In view of the facts above recorded, it appears that the name *cuprobismutite* has no mineralogical significance and may be discarded.

REFERENCES

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 PEACOCK, M. A., *Zeits. Krist.*, **86**, 203 (1933).
 SHORT, M. N., *U. S. G. S. Bull.* **825**, 104 (1931).
 WOLFE, C. W., *Am. Mineral.*, **23**, 790, (1938).

** Since the publication of this paper the elements have been changed to correspond to the dimensions of the unit cell. The *letters* used above for the forms are unchanged from the usage of the published table. The form *w* (121) has been reported by Wolfe (1938).

NOTES AND NEWS

ZONING IN SPHERULITES

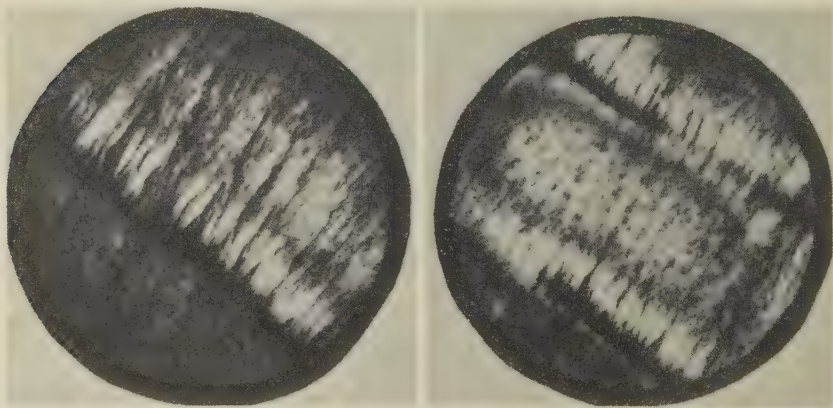
ARTHUR DAVID HOWARD,
New York University, New York.

INTRODUCTION

In studies of artificial spherulites, the author has observed the development of a peculiar type of zoning (Figs. 1 and 2). A similar phenomenon has been observed in nature by Whitman Cross in the spherulitic rhyolites of the Rosita Hills in Custer County, Colorado. So far as the writer is aware, Cross neither described nor illustrated this phenomenon in any of his own reports. Unfortunately, too, his original thin sections are no longer available. However, one of Cross' photographs of this structure appears in Iddings' *Igneous Rocks* (2nd edition, John Wiley and Sons, New York, 1920, p. 233) and is herewith reproduced as Fig. 3. The present paper is an inquiry into the origin of this zonal structure.

DESCRIPTION OF ZONING

The zoning consists of concentric shells of the crystallizing substance, but the transition from the outer surface of one shell to the next is peculiar. At some distance from the center of the menthol spherulite the radiating crystal fibers terminate to form a complete compact spherulite. On the surface of this spherulite other relatively thick crystal fibers appear at evenly distributed but scattered points. These fibers become more



FIGS. 1 and 2. Multiple zoning in menthol spherulites under crossed nicols. The core of the spherulite is to the lower left. Magnification about $24\times$.

slender outward and branch and ramify until they again form a massive, compact shell. From this surface the transition to still another shell may take place (Figs. 1 and 2). Iddings (*op. cit.*, pp. 232-233) in discussing Cross' illustration states that the photograph represents "a section across a large spherulite at a spot where a spheroidal surface, or zone, terminating closely parallel prismoids, minutely branched, is succeeded by a growth of larger, branched crystals. These in turn become slender and more nearly parallel to one another."

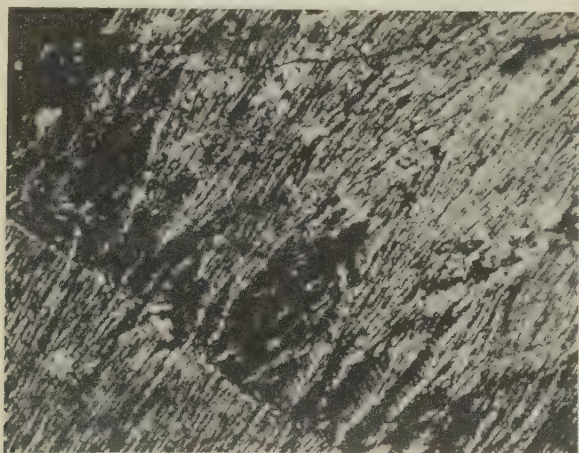


FIG. 3. Zonal boundary in spherulite from Rosita Hills, Colorado. (Cross, U. S. Geological Survey.)

ORIGIN OF ZONING

Iddings attributes the variation in the crystallization of the radiating crystals shown in Fig. 3 to "changes in saturation in the liquid magma arising from the rapidity of crystallization of the prismoid minerals." He suggests that "a sudden rush of crystallization may liberate sufficient heat to reduce the saturation of the surrounding liquid and even stop the separation of solid material until the diffusion of the heat permits saturation to rise again." He further notes that "a pulsation of crystallization in rapidly solidifying liquids can be observed in the laboratory under favorable circumstances."

In the explanation offered below for this type of zoning the writer makes use of the concepts of metastable and labile conditions in supercooled liquids. According to the more widely accepted of the two versions concerning the rate of crystallization in a supercooled liquid (Fig. 4),

namely that of Tammann,¹ and later Doelter,² crystallization in a slowly cooling, supersaturated³ solution will for some time take place slowly (metastable condition) from a few scattered loci, resulting in the growth of scattered large crystals. With continued fall in temperature the limit of supersaturation for the solution is finally reached, and copious crystallization from many centers results (labile condition). This may be the explanation for some porphyritic structures. The zoning described in this paper is more readily understandable on the basis of the curve subscribed to by Tammann and Doelter. Dr. Bowen⁴ writes that he is not entirely convinced that crystallization can take place under both metastable and

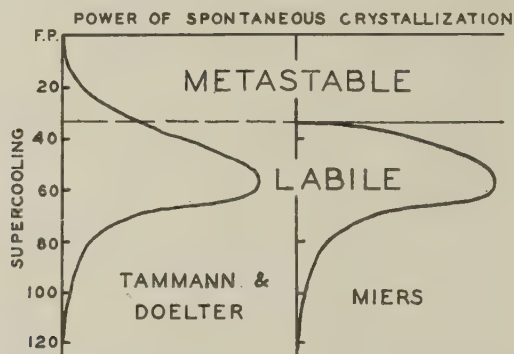


FIG. 4. Two concepts of the effects of supercooling on crystallization. Although Tammann experimented with organic substances and Doelter with rock-forming minerals, their conclusions were similar. The left-hand curve illustrates Doelter's results with augite. Miers' conclusions were based on experiments with salt solutions. The views of Tammann and Doelter are believed to more nearly represent conditions in magma. (From Harker's *Natural History of the Igneous Rocks*. Slightly modified.)

labile conditions. In his opinion crystallization under one set of conditions may preclude crystallization under the other. If this view should prove to be correct the explanation for zoning offered in this article would require revision. It is interesting to note that Mourant,⁵ in discussing a type of zoning characterized by concentric areas of silica and feldspar, has likewise employed the concepts of metastable and labile crystallization.

¹ Tammann, Gustav, *Kristallisieren und schmelzen*, J. A. Barth, Leipzig, 148-156 (1905).

² Doelter, Cornelius, *Physikalisch-chemische-mineralogie*, J. A. Barth, Leipzig, 111-112 (1905).

³ Both "supersaturation" and "supercooling" imply retarded crystallization. The former term, however, is best limited to solutions, whereas the latter includes simple melts.

⁴ Bowen, N. L., Personal communication.

⁵ Mourant, A. E., The spherulitic rhyolites of Jersey: *Mineral. Mag. and Jour. Mineral. Soc. London*, 23 (No. 139), 227-238 (1932).

Rate of cooling is probably the controlling factor in determining whether a compact or zoned spherulite will appear from solution. If the cooling is sufficiently rapid, the solution in the neighborhood of a center of crystallization may not linger at any temperature sufficiently long to permit all the material in excess of the saturation point for that temperature to crystallize out. In other words crystallization of the solute in excess of the saturation point for a given temperature may not yet be complete when an additional supply, representing the excess for the next lower temperature, begins to appear. Precipitation in this case will be continuous, and compact spherulites can be expected. If, however, the rate of cooling is slow, the solution may, under the conditions described later, periodically rid itself of the solute in excess of the saturation point for certain temperatures. The zoning described above is probably a result of such rhythmic precipitation.

The degree of saturation within cooling lava undoubtedly varies from point to point. If the cooling is slow enough, parts of the lava may become supersaturated. According to the experiments of Doelter who worked with rock-forming minerals (Fig. 4), crystallization would begin at a few scattered centers and its rate would be slow (metastable condition). When the limit of supersaturation was reached, the rate of crystallization would accelerate to a maximum and then diminish as rapidly (labile condition). The rapid extraction of solute would soon impoverish the solution around the crystallizing body, and crystallization would cease. The earlier formed crystals would thus be insulated from the rest of the magma by an envelope of barely saturated solution.

The features to be explained in zoned spherulites are the compact core and the successive concentric shells. On the assumption of an initial period of slow and scattered crystallization (metastable condition) the center of the core might be expected to show thick and widely spaced crystal fibers. If the central fibers in menthol spherulites are thicker than the outer ones, it is not readily apparent. Certainly they are not widely spaced. However, conditions at the core of a spherulite are necessarily peculiar; crystallization in the outer shells takes place over a spherical surface of large radius, whereas this area diminishes toward a point at the center of the spherulite. Hence, no matter how little material crystallizes out under metastable conditions at the center of the core, there is so little room that it completely occupies the space available. A relatively large amount of solute can hardly be expected to crystallize from scattered centers in the restricted area at the center of a spherulite. Hence, the metastable crystallization at the center may not be distinct from the succeeding, more rapid, labile crystallization of the outer part of the core.

The rapid labile crystallization may impoverish the magma in contact with the spherulite of the constituents needed for further growth. The saturation of the surrounding solution may also be lowered by an increase in temperature due to the heat of crystallization and also, in the case of solutions, by the relative increase in water due to extraction of the solid phase in the growth of the spherulite. It is probable, therefore, that the solution immediately surrounding the spherulite at this stage is no longer supersaturated. Crystallization will then cease, and the compact core of the spherulite will terminate in a spherical surface.

Crystallization will not be resumed until the immediately surrounding solution again becomes supersaturated. Later crystallization will also take place under metastable and labile conditions. From the solution surrounding the compact core crystallization will start at scattered loci⁶ on the earlier formed spherulite front (metastable condition). As the temperature falls, the solution will pass slowly through the metastable phase with crystallization slowly increasing in volume as reflected in the fan-like branching of the feldspar fibers (Fig. 3). When the temperature falls sufficiently, the solution will reach the limit of supersaturation, and here crystallization will be spontaneous (labile condition). This is reflected in the spherulite by the more rapid branching of the feldspar fibers to give for the second time a solid spherulite front. This process, involving periodicity of crystallization, may continue until a multi-zoned spherulite results.

ACKNOWLEDGMENTS

The writer is greatly indebted to Dr. N. L. Bowen for examination of the manuscript.

⁶ Viscosity may explain the failure of the earlier formed crystals to inoculate the enveloping solution and cause spontaneous crystallization.

OPTICAL EVIDENCE OF POLYSYNTHETIC TWINNING IN
ARSENOPYRITE

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ABSTRACT

Crystal structure determinations have shown that arsenopyrite is monoclinic rather than orthorhombic. It was necessary to postulate mimetic twinning of polysynthetic twins to account for its pseudo-orthorhombic diffraction effects and symmetry. This twinning has been observed on polished sections under polarized light. The attitude of the twins precludes orthorhombic symmetry.

It has been shown elsewhere by Buerger¹ that the minerals of the arsenopyrite group having a general formula $AB'B''$ are superstructures based on the marcasite structure and have the symmetry of the space group C_{2h}^5 . In order to account for the apparently orthorhombic diffraction effects observed in rotation and Weissenberg photographs, and the orthorhombic symmetry of individual crystals, it was necessary to postulate the existence of mimetic twinning. It is the purpose of this paper to present in a formal manner corroborative evidence of an optical nature which was mentioned by Buerger² and which demonstrates the validity of the twin hypothesis.

Twinning was apparently observed by Scherer³ as a result of etching the brachydome of arsenopyrite crystals. Scherer interprets his results as follows:

The condition that there appears on the base four compartments which behave equally indicates twin formation. This presupposes the assumption of asymmetrical individuals and therefore has little claim on truth. It was clear to me that probably the etch lines result from varying degrees of solubility of the component parts of the crystal, a supposition which forced the hypothesis of a layer synthesis of the arsenopyrite. . . .

This interpretation will be shown to be incorrect.

Small single crystals of arsenopyrite were polished in several orientations by means of a polishing device especially designed for the purpose. The apparatus and method of preparing polished sections in predetermined orientations have been described.⁴ Briefly, the crystal is cemented to an adjustable head which fits both the two-circle goniometer and the polishing machine, oriented on the goniometer in the desired manner and transferred to the polishing machine. The cut is made by a rotating wheel covered with emery paper, and it is polished with dry chrome on linen.

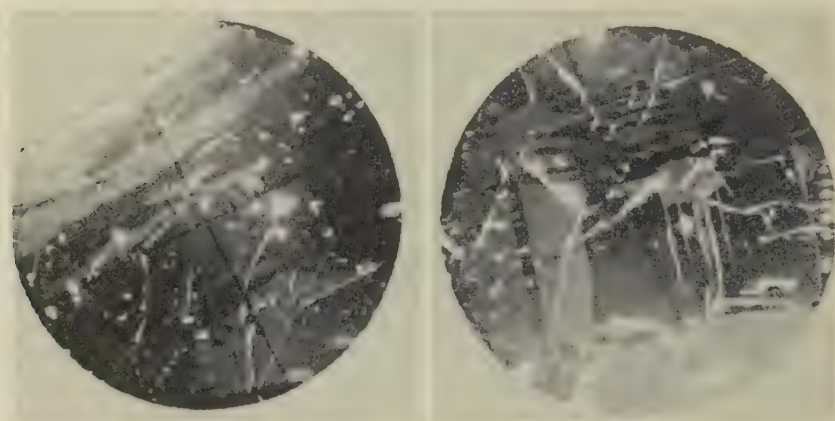
¹ Buerger, M. J.: *Zeits. Krist.*, (A) **95**, 83-113 (1936).

² Buerger, M. J.: *Op. cit.*, 95-96.

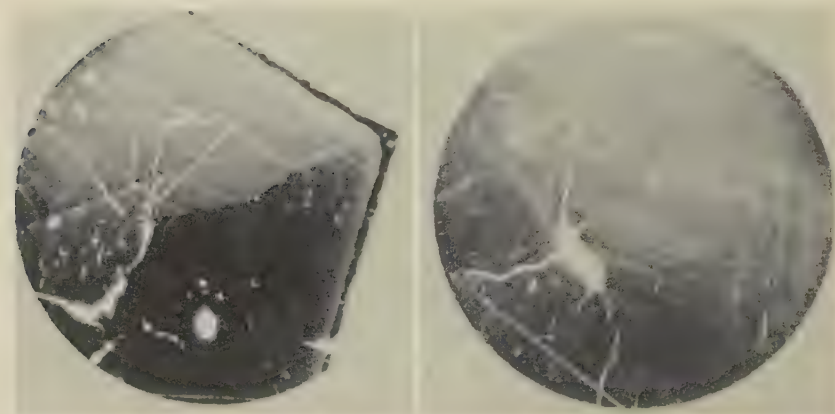
³ Scherer, F.: *Zeits. Krist.*, **21**, 354-387 (1892).

⁴ Buerger, M. J., and Lukesh, J. S.: *Am. Mineral.*, **21**, 667-669 (1936).

A number of sections were cut in various orientations on crystals from different locations. Specimens from Spindelmuhle and Saxony (?) in Germany, and Sulitjelma, Norway, as well as a large crystal of unknown origin all showed polysynthetic twinning under the polarizing microscope.



FIGS. 1 and 2. Surface of Sulitjelma crystal nearly parallel to (001). Crossed nicols. $\times 64$.



FIGS. 3 and 4. Surface of Spindelmuhle crystal nearly parallel to (001). Crossed nicols. $\times 60$. All crystallographic notation referred to the old arsenopyrite orientation.

The accompanying illustrations (Figs. 1-4) are photomicrographs of cuts on two crystals. Figures 1 and 2 are on a crystal from Sulitjelma and 3 and 4 on one from Spindelmuhle.

CRYSTALS FROM SULITJELMA

The cut illustrated is nearly parallel to (001). Figures 1 and 2 are different parts of the same surface, the edge shown in Fig. 1 being the intersection of the cut with a dome face. The cross-hairs indicate the directions of the a and b -axes, with the a -axis parallel to the dominant twin direction. The attitude of the twin planes was determined from these cuts and others in different orientations. The twins which are seen parallel to the a -axis in a cut normal to the c -axis were found to be parallel to (011). Those in the direction of the b -axis were found also to be dome twins, making an angle of about thirty-seven degrees with (100). The (011) twins were in all cases the dominant ones.

CRYSTALS FROM SPINDELMUHLE

Figures 3 and 4 are parts of the same surface cut nearly parallel to (001). The angle in Fig. 3 is the junction of ($\bar{1}\bar{1}0$) and ($\bar{1}10$) and the light and dark areas are the individuals of a twin. The extinction effects observed on this and all other cuts preclude the composition hypothesis of Scherer. If the etch results were due to a layer synthesis, the areas which are sharply contrasted would be equivalent and would extinguish coincidentally. In Fig. 4 there can be seen the center of the crystal with two sets of twin boundaries at right angles to each other. From this and other cuts the twin planes were found to be parallel to (100) and (010). These two sets of twin planes divide the base of the crystal into the four areas noted by Scherer on etching the brachydome. Each of the four areas is also twinned parallel to the prism faces, a form of twinning analogous to that found in the Sulitjelma crystals. On the basis of the latter type of twinning, a re-orientation of the Spindelmuhle crystals seems indicated, interchanging the a and c -axes. All crystallographic notation used in this discussion is referred to the conventional arsenopyrite orientation.

Preliminary observations were also made on crystals of manganite. Twinning was found, but it was not studied in detail. The inference from this is that twinning can be expected in other members of the arsenopyrite group.

From a crystal structure point of view, the pinacoid twins found in the Spindelmuhle crystals are the most important. The pinacoids of two of the three orthorhombic space groups to which arsenopyrite might be assigned from x -ray diffraction data are symmetry planes. Since twinning cannot occur on a symmetry plane, these two space groups must be discarded. The third possible orthorhombic space group can be eliminated and the monoclinic nature established by reasoning which is beyond the scope of this paper.⁵

⁵ Buerger, M. J., *Op. cit.*

CONFERENCE ON APPLIED NUCLEAR PHYSICS

October 28–November 2, 1940

A general Conference on Applied Nuclear Physics, sponsored by the American Institute of Physics in cooperation with the Massachusetts Institute of Technology, will be held during the week of October 28–November 2, 1940, at the Massachusetts Institute of Technology, Cambridge, Massachusetts. The rapidly increasing number of applications of methods and apparatus characteristic of nuclear physics in the fields of biology, radiology, chemistry, geology, and industrial physics has long emphasized the usefulness of a joint conference between physicists and their colleagues in other fields of science.

The purposes of the Conference are to bring together investigators who may be widely separated geographically, and to provide a forum for assembling and correlating present knowledge and difficulties, and for directing attention toward fundamental lines of research which should be the subject of future investigations.

The week's activities will be divided into separate sessions on applications to biology, chemistry, radiology, metallurgy, geology, and to general sessions relating to the production and use of radioactive and stable isotopes, and the protection of workers from radiation. An outline of the general program is given in the following table:

CONFERENCE ON APPLIED NUCLEAR PHYSICS

Digest of Program

Monday A.M., October 28, 1940 (two parallel sessions)

Geology I: "Techniques and Standards in Terrestrial Radioactivity Measurements."

Metallurgy I: "Tracer Studies of Metal Diffusion and Corrosion."

Monday P.M., October 28, 1940 (two parallel sessions)

Geology II: "Geochemical Applications of Radioactivity."

Metallurgy II: "Radiography with Gamma-Rays, X-Rays, and Neutrons."

Tuesday A.M., October 29, 1940 (three parallel sessions)

Geology III: "Radioactive Methods of Geologic Age Determinations."

Chemistry I: "Tracer Techniques in General Chemistry."

Radiology I: "General Aspects of Cancer Therapy."

Tuesday P.M., October 29, 1940 (three parallel sessions)

Geology IV: "Geophysical Applications of Nuclear Physics."

Chemistry II: "Tracer Techniques in Analytical Chemistry."

Radiology II: "Radium and Roentgen Therapy."

Wednesday A.M., October 30, 1940

General I: "Production of Radioactive and Stable Isotopes and of Penetrating Radiations."

Wednesday P.M., October 30, 1940

General II: "Measurement of Radioactive and Stable Isotopes and of Penetrating Radiations."

Thursday A.M., October 31, 1940

General III: "Protection of Workers from Biological Effects of Radiation."

Thursday P.M., October 31, 1940 (three parallel sessions)

Chemistry III: "Synthesis of Organic Substances Containing Tracers."

Radiology III: "Neutron and Artificial Radioactivity Therapy."

Biology I: "Tracer Techniques in Biology."

Friday A.M., November 1, 1940 (two parallel sessions)

Radiology IV: "Dosage Measurements."

Biology II: "Tracer Studies of Plant and Animal Metabolism."

Friday P.M., November 1, 1940 (two parallel sessions)

Radiology V: "Radiobiology."

Biology III: "Tracer Studies" (continued).

Saturday A.M., November 2, 1940 (two parallel sessions)

Biology IV: "Tracer Studies" (concluded).

General IV: "Contributed Papers."

COMMITTEE IN CHARGE OF PROGRAM

Robley D. Evans, *Chairman*
Massachusetts Institute of Technology

ELMER HUTCHISSON, *Secretary*
University of Pittsburgh

HENRY A. BARTON
American Institute of Physics

EDW. U. CONDON

Westinghouse Electric & Manufacturing
Company

LEE A. DUBRIDGE
University of Rochester

G. FAILIA

Memorial Hospital, New York

CLARK GOODMAN

Massachusetts Institute of Technology

ERNEST O. LAWRENCE

University of California

HAROLD C. UREY

Columbia University

The daily sessions will consist of short invited papers by leading investigators followed by vigorous and searching discussion by the conferees. Ample time will be allowed between and after regular sessions for personal and informal conferences. While the emphasis will be on the program of invited papers and the discussion of these, provision has also been made for a limited number of ten-minute contributed papers. Five one-hour evening sessions will be held, in each of which an outstanding investigator will summarize the status of the several fields which are joined together by the Conference. The evening lectures will be open to the general public.

Anyone who can actively participate in or profit by the Conference is eligible and cordially invited to become a member. Advance registration (no fee) will be required to permit suitable arrangements to be made. Those wishing to attend should register by letter as soon as possible and not later than October 1. Letters and inquiries should be addressed to Professor Robley D. Evans, General Chairman, Conference on Applied Nuclear Physics, Massachusetts Institute of Technology.

NOMINATIONS FOR OFFICERS OF THE MINERALOGICAL
SOCIETY OF AMERICA FOR 1941

The Council has nominated the following for officers of the Mineralogical Society of America for the year 1941:

PRESIDENT: Fred E. Wright, Geophysical Laboratory, Washington, D. C.

VICE-PRESIDENT: William J. McCaughey, Ohio State University, Columbus, Ohio.

SECRETARY: Paul F. Kerr, Columbia University, New York, N. Y.

TREASURER: Earl Ingerson, Geophysical Laboratory, Washington, D. C.

EDITOR: Walter F. Hunt, University of Michigan, Ann Arbor, Michigan.

COUNCILLOR: (1941-1944): Martin A. Peacock, University of Toronto, Toronto, Ontario, Canada.

ANNOUNCEMENT OF ANNUAL MEETING

The twenty-first annual meeting of the society will be held in Austin, Texas, December 26-28, 1940, in connection with the 52nd meeting of the Geological Society of America. The headquarters of the Geological Society will be at the University of Texas, and the scientific sessions and social functions will be held both at the University and the Stephen A. Austin hotel.

Members of the society who are planning to present papers at the scientific sessions of the annual meeting should notify the secretary as soon as possible in order to receive the proper blanks for their abstracts. All abstracts should be in the secretary's office by *November 1st*.

Advance announcement of the annual meeting will be distributed to members of the society, along with the ballot for officers, the middle of October. The final program of the meeting, including the schedule of papers, abstracts, and other information will be sent to each member in December. Further specific information regarding the annual meeting may be obtained from the secretary's office.

PAUL F. KERR, *Secretary*

Dr. A. E. Alexander, formerly industrial fellow at the Mellon Institute of Industrial Research, Pittsburgh, Pa., is now located in New York city, where he has charge of the gem and pearl testing laboratory, sponsored by a group of New York retail and wholesale jewelry houses. The laboratory is known as the Bureau of Natural Pearl Information, and is located in the Frances Building, 665 Fifth Avenue.

The body of Dr. John Eliot Wolff, professor emeritus of petrography at Harvard, was found after a twenty-seven hour search on August 12 beside his stalled automobile in the Mohave Desert, California. Death was probably due to thirst and exhaustion. Dr. Wolff had started from his Pasadena home for a one-day survey of Mint Canyon. He was eighty-two years old. Dr. Wolff was President of The Mineralogical Society of America in 1934.

Dr. Philip Krieger, assistant professor of geology at Columbia University, was killed in an automobile accident on August 18, while driving to Gouverneur from North River, New York. Professor Krieger was thirty-nine years of age.

BOOK REVIEW

ANTARCTICA. By GRIFFITH TAYLOR. Regionale Geologie der Erde. Bd. 1, Die alten Kerne, Abschnitt VIII, 34 pp., index. 11 figs. Akademische Verlagsgesellschaft, Leipzig, 1940. Price 7.80 RM.

Dr. Taylor has attempted the difficult task of bringing together data pertaining to observations on the geology of the Antarctica, a continent with an approximate area of 5,100,000 square miles, excluding the Ross Shelf Ice.

Chapter I deals with the relation of Antarctica to other continents. An attempt is made to correlate the great structural features of South America and Australia with structural, or supposed structural features, of Antarctica. A continuation of the Antarcticandes through Antarctica to New Zealand is suggested by Dr. Taylor. He suggests that the Artesian geosyncline in Australia corresponds with the theoretical great downfold extending from the Ross to the Weddell Seas and is the counterpart of the La Plata depression of South America. Chapter II is one on the areal geology of East Antarctica in the region of the Great Fault Scarp. A brief statement is made of the stratigraphy of East Antarctica and the Palmer Land (West Antarctica) region, and a rapid survey is given of the detailed geology of special areas. Chapter III deals briefly with the areal geology of the coasts south of the Indian Ocean and south of Africa. Chapter IV treats of the areal geology of West Antarctica. A brief statement is made about the Edsel Ford Ranges, Marie Byrd Land, and four pages of text review the research of the Swedish Antarctic Expedition, 1901-03. Chapter V describes Antarctic physiography and includes a discussion of the general features of erosion under polar conditions with special reference to the ice-forms and land-forms which are characteristic of the Antarctic Continent. The discussion is concerned principally with the ice of South Victoria Land. Chapter VI is a summary. There is one page of bibliography, and an index of some five pages of authors, fossils, places, and terms.

Suggested corrections in the figures and text are as follows. In Fig. 2, Peter Isle should be Peter I Island, and Mt. Nansen, Mt. Fridtjof Nansen. Ellesworth should be spelled Ellsworth. In Fig. 3, Edsel Ford Range should be changed to Edsel Ford Ranges, and Mt. Haines to Haines Mts. In Figs. 4 and 10, MacMurdo Sound should be McMurdo Sound. In Fig. 7, Rea Mts. should be Mt. Rea, and Fosdick Mt., Raymond Fosdick Mts.

Ellesworth should be spelled Ellsworth on pages 2, 3, 6 and 7. A statement on page 7 is incorrect. Stewart (*Proc. Am. Phil. Soc.*, 1934) did not deny that the rocks of Marie Byrd Land should be classed with the Andean rocks. In fact, this article dealt not with Marie Byrd Land specimens, but with rocks from South Victoria Land. On pages 8 and 15, reference is made to Mount Nansen, when it should be Mount Fridtjof Nansen. Mount Nansen is in the Terra Nova Bay region, South Victoria Land, and Mount Fridtjof Nansen is in the Queen Maud Mountains, S.V.L. McMurdo Sound and MacMurdo Sound are used interchangeably. McMurdo is correct. On page 19, in referring to the Edsel Ford Ranges, the statement is made, "The series of younger folded sediments found in the Queen Maud area is entirely wanting." As far as is known, there are no "younger folded sediments" in the Queen Maud Mountains. On pages 20-24, there is a discussion of the pre-Tertiary and Tertiary rocks of West Antarctica. The data presented is a review of the work done by the Swedish explorers and no reference is made to the findings of the *Expédition Antarctique Belge, 1897-99*, *Expédition Antarctique Française, 1903-05*, and *1908-10*, and the British Graham Land Expedition, 1934-37, in West Antarctica. On page 34, Nordenskiöld should be spelled Nordenskjöld.

In one instance apparently the original scientific reports of an expedition were not consulted. On page 18, a paper by Priestley and Tilley is referred to instead of Reinisch's "Petrographische Beschreibung der Gaussberg-Gesteine."

DUNCAN STEWART, JR.

NEW MINERAL NAMES

Stiepelmannite

PAUL RAMDOHR AND E. THILO: Stiepelmannite, ein neues Mineral der Hamlinitgruppe mit Yttrium und seltenen Erden. *Centr. Mineral. Abt. A*, Nr. 1, 1-8, 2 figs., 1940.

NAME: For Mr. Stiepelmann, owner and operator of the Klein Spitzkopje property, who furnished the material.

CHEMICAL PROPERTIES: A phosphate of aluminum and yttrium earths. Formula $\text{YPO}_4 \cdot \text{AlPO}_4 \cdot 2\text{Al}(\text{OH})_3$. Analysis: SiO_2 0.29, X_2O_3 29.25, ZrO_2 1.12, CaO 0.50, Al_2O_3 30.83, H_2O 11.07, P_2O_5 (by difference) 26.94; Sum 100.00. Attacked with difficulty by concentrated hydrochloric acid.

CRYSTALLOGRAPHIC PROPERTIES: Trigonal. Habit rhombohedral, resembling modified cubes. $c = 1.272$. Forms $(10\bar{1}1)$, (0001) , $(02\bar{2}1)$. $a = 6.75 \text{ \AA}$, $c = 16.52 \text{ \AA}$.

PHYSICAL AND OPTICAL PROPERTIES: Colorless to pale wine yellow. Luster high. $H = 6$. Fracture conchoidal. Cleavage (0001) and $(11\bar{2}0)$ indistinct. $G = 3.671\text{--}3.713$. Uniaxial, positive. $\omega = 1.695$, $\epsilon = 1.705$.

OCCURRENCE: Found in small crystals, coated with hyalite and limonite upon albite, microcline, fluorite, etc., from the beryl pegmatites of Klein Spitzkopje, South West Africa.

REMARKS: Stiepelmannite is a member of the alunite-jarosite group and is closely related to florencite.

W. F. FOSHAG

DISCREDITED SPECIES

Kreuzbergite (= fluellite)

A. SCHOLZ AND H. STRUNZ: Identität von Kreuzbergite mit Fluellite. *Centr. Mineral. Abt. A*, Nr. 6, 133-137 (1940).

Reexamination of kreuzbergite shows it is not a phosphate, but from its optical, crystallographical and Debye-Scherrer diagrams is fluellite $\text{Al}(\text{F}, \text{OH})_3 \cdot \text{H}_2\text{O}$.

	Stenna Gwyn	Hagendorf	Pleystein	Königswart
α	1.475	1.490	1.489	
β	1.490	1.496	1.495	
γ	1.510	1.509	1.506	
a	0.770	0.7724	0.7485	0.7516
c	1.874	1.8715	1.9008	1.7794

The variations are explained as due to isomorphous replacement of (F) by (OH.)

W. F. F